ChemEd

EDITORIALLY SPEAKING

Recommendation for the Preparation of High School Teachers of Science and Mathematics—1959" is the title of an important report recently issued by the Cooperative Committee of the AAAS. (See *School Science and Mathematics*, **LIX,** 218, 1959 (April). The document deserves careful study by all who are concerned with the establishment of certification requirements for teachers in the schools of the nation. It is a carefully prepared report and proposes a workable program. We see it as one of the most realistic statements that an organization speaking for professional scientists has devised. It will be a weapon in the hands of those who are fighting the battle of assuring subject-matter competence in the training of science teachers.

Adequate training of a science teacher must reflect the following factors (we quote):

> Sciences have advanced in the last ten years. Word of new advances spreads by newspapers, magazines, and television. This stimulates questions by the curious students. Teachers must be prepared to stimulate further the interest in such questions, to provide sound answers for them, and to direct effective reading at the level of the student's background. The course work taken by the teachers should prepare them to keep up to date.
>
> A concerted move was made (beginning in 1954) by a number of colleges and universities of this country to work with secondary schools in developing college-level courses for their most able students. In chemistry, the time-equivalent of at least three semesters permits instruction at the college level, using college texts. Thus students qualify for sophomore courses on college entrance thereby reducing duplication.
>
> More and more of the colleges and universities are emphasizing demonstrated proficiency in subject-matter areas rather than simply permitting entrance to the college with "sixteen" high school credits. Some kind of entrance examination as part of the method of selecting students is being adopted.
>
> The increased complexity of the fields of science emphasizes the importance of content material to make it possible for the teacher to answer the "why" type of question rather than to just teach the material empirically.

The report continues by acknowledging realistically other pertinent considerations. These are the several conflicting circumstances often overlooked by the "hatchet wielders" among the critics of present regulations. The carefully worded statement is:

> Most science teachers are required to teach several sciences including, perhaps, a course in general science, rather than just one science. This means that a teacher must have depth of preparation in a variety of areas.
>
> Because of the impact of science on other areas, the science teacher should have preparation in the social sciences and humanities to help give him the kind of perspective that the top-rate scholar and citizen needs.
>
> There are certain elements in professional education which should be helpful in giving the best performance in the classroom. These elements may be provided by courses in such areas as the psychology, philosophy, and methodology of education and especially by experience in student teaching.

The real meat of the document is contained in the specific recommendations for distribution of credit in the prospective teacher's academic training. These spell out a re-affirmation of the preliminary 1946 version of the committee's stand: *One half of the four year program should be devoted to science courses.* This would leave at least 60 semester hours for courses in the humanities, social sciences, and professional education. *Colleges and certification authorities should work toward a five-year program which would allow the teacher further to build subject-matter competence.* This implies that all courses in the undergraduate major and supporting sciences be the *basic courses including laboratory work and not "survey" courses.*

The suggested preparation for teachers whose speciality will be chemistry is as follows: 28 credits in chemistry, including physical chemistry, 12 in mathematics, 8 each in physics and biology, and 3 in earth science. To this total of 59 could be added the 30 of a fifth year: 18 in chemistry, to be chosen from such advanced work as systematic inorganic chemistry, biochemistry, and radiochemistry, and 6 each in mathematics and physics.

Other typical programs are suggested which will provide sensible compromise concentrations for those who anticipate teaching more than one subject. For example a physics-chemistry combination would be: physics 18, chemistry 18, mathematics 13, biology 6, and earth science 5.

The report does not suggest the creation of a "general science" major but does outline a possible program to train that much-needed future teacher of junior high school science. Adequacy should be attained by a program containing 10 biology, 8 chemistry, 12 physics, 6 earth science, 6 mathematics, and 18 credits of upper division work in two areas.

No reader of this page can be unconcerned about the problem to which the work of this committee has been addressed. All should become informed on their local situation and lend their support to efforts for improvement. The report here quoted, offered in a spirit of genuine cooperation without desk-pounding in favor of a special interest, should help us go far toward the goal of all citizens: better education for the youth of the nation.

Donald R. Martin
Olin Mathieson Chem. Corp.
Niagara Falls, New York

The Development of Borane Fuels

In the last several years, several reviews on the chemistry of boron have been written (*33*, *36*, *39*) and many articles have appeared in newspapers and nonchemical journals concerning the use of boron compounds in fuels.

Since the Second World War, we have all become more aware of boron and its compounds. First, we heard of the utilization of boron by the Atomic Energy Commission and of the construction of plants to produce boron isotope, B^{10}. The fact that the layman has heard of boron isotopes and yet has not always understood the expression is exemplified by the report that someone had inscribed with chalk on a brick wall in the lower East Side of New York City: "Johnnie Smith is a boron isotope" (*27*).

Secondly, we have become aware of the application of boron compounds to fuels because of the intensive advertising campaigns of the gasoline producing companies in several of our states. In these areas, it is common to see boron advertised in large banners at each of the companies' service stations. In automobile fuel, boron compounds, such as alkyldihydroxyboranes, are added in relatively small amounts to gasoline (*11*). As the result of using these boron compounds as additives, better performance is claimed for the piston engine of the automotive industry.

We are aware also of the use of boron compounds, such as the alkyl boranes, as the so-called exotic or high energy fuels. In this application, the alkyl borane is the fuel itself and is not an additive. Quite naturally the question arises, why is a high energy fuel required? To answer this question, it must be stated first that the high energy fuels may be used in air-breathing jet engines and rocket engines, both of which have different fuel requirements than the internal combustion engine.

It is desired to have the jet planes and the missiles carry a greater pay load a greater distance. To carry a greater load a greater distance may be more easily achieved by going higher. However, to go farther and higher may necessitate attaining a greater speed during flight. As a consequence, more stringent fuel properties are required in order that the plane or missile may go farther, higher, and faster.

To go farther requires more energy per pound of fuel coupled with a higher combustion efficiency in the engine.

If the vehicle is to go higher, the fuel must have (*a*) a faster flame speed (to prevent a flame-out at high altitude and the accompanying low pressure) and (*b*) a low vapor pressure (to prevent appreciable loss of fuel at the high altitude by evaporation).

To go faster, the vehicle requires a fuel with (*a*) a high combustion efficiency in a high velocity air stream and (*b*) a stability at fairly high temperatures. The greater stability is required because the surface of the vehicle and the fuel tanks become hot when the vehicle is traveling a speed several times faster than sound (mach numbers). In summary, a high energy fuel has to have a high heat of combustion, a low vapor pressure, thermal stability, high density, and a high flame speed plus the physical properties necessary to insure its safe handling during manufacture, shipping, and storage.

In 1952 the Department of Defense made chemical industry aware of its need for better high energy fuels. No limitations were placed on the chemical industry with regard to which atoms, molecules, or mixtures thereof might be used to synthesize an improved high energy liquid fuel. Table 1 shows fuels available at that time.

Table 1

Fuels	Btu/lb
Liquid hydrogen	52,470
Pentaborane(9)	29,961
JP-4	18,605

JP-4 is a kerosene-rich hydrocarbon fuel which is used by jet planes. Pentaborane(9) had been investigated for application in jet and rocket engines. The heat of combustion of pentaborane(9) is attractive, but the fact that it is pyrophoric, toxic, and has a low density reduces its usefulness considerably. Liquid hydrogen has the highest heat of combustion of any material and therefore represents the ultimate in a fuel. However, its low density and low boiling point introduce problems of handling and storage which make its use on a large scale quite difficult.

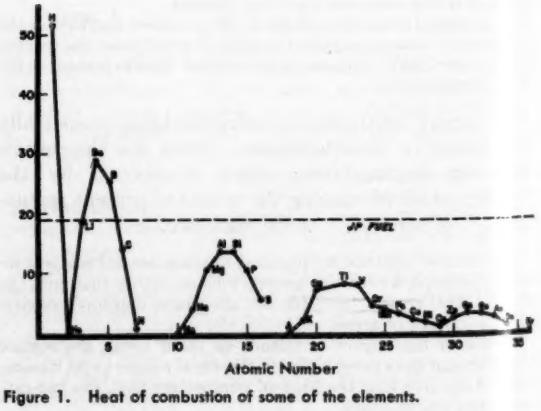


Figure 1. Heat of combustion of some of the elements.

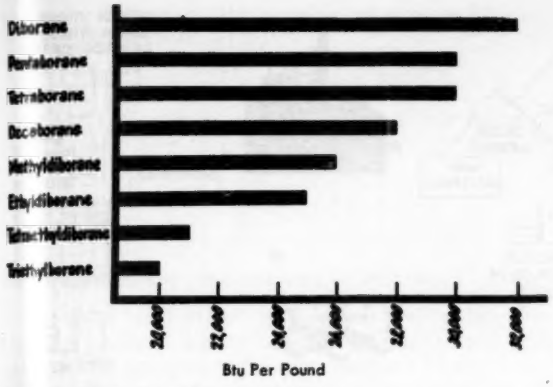


Figure 2. Heat value of borane propellants.

To begin the search for a better high energy fuel, the chemists naturally turned to the periodic table. Accordingly, Figure 1 was constructed in which the heat of combustion of each element, when burned with oxygen, is plotted against its atomic number. As discovered by Lothar-Meyer and Mendeleev many years ago, the principle of periodicity applies. As a criterion for selecting candidate elements from which to synthesize a new fuel, the values on the curve are compared with the horizontal dotted line which represents the heat of combustion of the JP fuels. It is seen that a better fuel may be prepared only if hydrogen, beryllium, or boron are used as the "building blocks." As indicated above, certain physical properties of hydrogen render it impractical, and beryllium was eliminated because of its limited availability, toxicity of its compounds, and the fact that no liquid compounds of beryllium were known. Consequently, boron and its hydrides were selected as the materials from which the synthesis of a better high energy liquid fuel would be attempted.

The three most common boranes known at that time were diborane, pentaborane(9), and decaborane. Under standard conditions, diborane is a gas, decaborane is a solid, and pentaborane(9) is a liquid with certain unsuitable properties as mentioned previously. However, since the heat of combustion of each of these three compounds is attractive, it was predicted that these molecules might be modified in some way to convert them to liquid compounds with the desired properties without losing much of their energy content. The heats of combustion of these boranes are shown in Table 2.

Table 2

Fuels	Btu/lb
Diborane	32,377
Pentaborane(9)	29,961
Decaborane	28,220

Referring to Figure 1, it is obvious that the candidate fuel molecule should contain boron and as much hydrogen as possible. A third element, having a high energy, is required to modify the borane to produce the other desired properties. Because of its scarcity and toxicity, beryllium was eliminated from consideration as a modifying element. The next best elements are either lithium or carbon. Because hydrocarbons are fuels and because all of the chemistry of organic synthesis is available for utilization, it was decided to attempt to modify the boranes by introducing a small quantity of carbon into them. The difficulty of achieving this without appreciably altering the heating value of the resulting molecules is shown in Figure 2. For example, the heat of combustion of diborane is 32,377 Btu/lb and the heat of combustion of methyldiborane is 26,420 Btu/lb. It is apparent that the replacement of one hydrogen of diborane by the smallest hydrocarbon group, i.e., the methyl group, results in a diminution of the heat of combustion of the parent borane of at least 15%. For comparison, Figure 2 indicates the deleterious effect of introducing more carbon into diborane to give ethyldiborane, tetraethyldiborane, and finally, triethylborane.

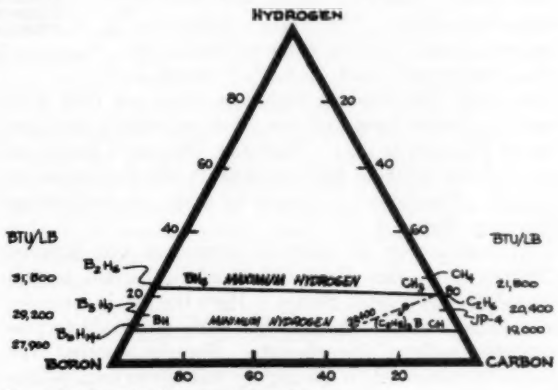


Figure 3. Boron-hydrogen-carbon system.

To understand the problem better and to serve as a guide for research, the ternary boron-hydrogen-carbon system shown in Figure 3 was developed. Recalling that the fuel should contain as much hydrogen as possible, and leaving one of the four co-valences of boron and carbon for bonding, a tie line was drawn on the diagram from a point representing the composition of BH_3 on the boron-hydrogen axis to a point representing the composition of CH_3 on the carbon-hydrogen axis. Obviously, this line represents the maximum amount of hydrogen that the resulting fuel molecule can have. By similar reasoning, insisting that at least one hydrogen must be attached to each boron and carbon atom, a tie line was drawn from the composition representing BH on the boron-hydrogen axis to a point representing composition CH on the carbon-hydrogen axis. This tie line represents the minimum amount of hydrogen in the synthetic fuel molecule. The next step was to plot on the diagram the points for molecules for which heats of combustion were known. For example, the heat of combustion of ethane and of triethylborane is approximately 20,400 Btu/lb. Therefore, a dotted tie line drawn from ethane through the point representing triethylborane indicates the compositions of matter whose heats of combustion should be very close to 20,400 Btu/lb. By drawing tie lines representing higher values for the heats of combustion, areas were described for compositions of car-

bon, boron, and hydrogen which would give the desired heats of combustion. Thus, empirical formulas for desired molecules were obtained. The next, and most difficult, step in the development of a high energy fuel was the synthesis of molecules whose compositions satisfied these theoretically derived empirical formulas.

For security reasons the processes used to make high energy fuels cannot be disclosed. However, to the extent possible, the related chemistry of the main steps in converting a boron ore into a high energy fuel will be discussed in accordance with the flow diagram depicted in Figure 4.

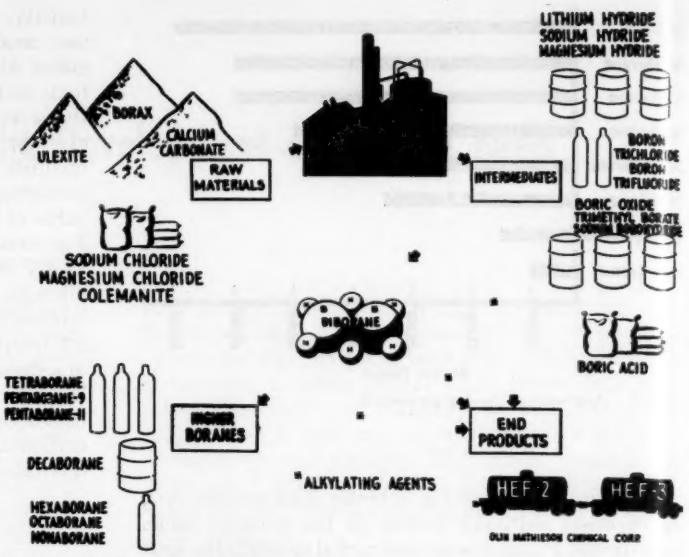


Figure 4. Synthetic routes to end products.

Conversion of Ore to Intermediates

The principal ores of boron are borax, $Na_2B_4O_7 \cdot 10H_2O$, kernite, $Na_2B_4O_7 \cdot 4H_2O$, colemanite, $Ca_2B_6O_{11} \cdot 5H_2O$, and ulexite, $NaCaB_5O_9 \cdot 8H_2O$. The world's largest deposit of borax is in the Kramer District in the southeastern part of Kern County in California. The Kramer deposit is about one mile wide and four miles long and contains ore which averages about 75% borax (*14*). However, this ore is under an overburden of 300 to 400 feet of shale which must be removed. The borax is mined by open pit methods as shown in Figure 5.

Approximately 50 miles northeast of the Kramer District is Searles Lake which is the second largest deposit in the United States. Here the ore is removed as a brine which is treated with carbon dioxide to precipitate sodium bicarbonate. Simultaneously, the borax is converted to the highly soluble sodium pentaborate, $Na_2B_{10}O_{16}$. After the sodium bicarbonate has been removed by filtration, raw brine is added to the solution to adjust the alkalinity to the point where all of the boron is present as sodium tetraborate. The solution then is allowed to cool and the sodium tetraborate precipitates and is removed by filtration (*14*).

The next step in a process for the production of high energy fuels is concerned with the conversion of borax to one of the three key intermediates, i.e., sodium borohydride, boron trichloride, and boron trifluoride.

The classical method for the conversion of borax to boric acid and thence to boric oxide is represented by the equations:

$$Na_2B_4O_7 \cdot 10H_2O + 2H_2SO_4 \rightarrow 4H_3BO_3 + 2NaHSO_4 + 5H_2O$$
$$2H_3BO_3 \rightarrow B_2O_3 + 3H_2O$$

An alternative process involves the substitution of the Lewis-type acid, ammonium chloride, for the sulfuric acid, thus:

$$5Na_2B_4O_7 \cdot 10H_2O + 10NH_4Cl \rightarrow 4NH_4B_5O_8 \cdot 4H_2O + 10NaCl + 6NH_3 + 37H_2O$$
$$2NH_4B_5O_8 \cdot 4H_2O \rightarrow 5B_2O_3 + 2NH_3 + 9H_2O$$

The advantage of this process is the utilization of the ammonium chloride liquor from the ammonia-soda process for the beneficiation of the borax. The captive ammonia is thus made available for recycle to the ammonia-soda process (*40*).

Having obtained boric oxide, binary boron compounds may be prepared at high temperatures by allowing the oxide to react with other elements to produce borides (*19*) according to the equations:

$$2B_2O_3 + 7C \rightarrow B_4C + 6CO$$
$$B_2O_3 + 4Mg \rightarrow MgB_2 + 3MgO$$

One of the key intermediates in the manufacture of boranes, boron trichloride, may be obtained from boron carbide or boric oxide by the reactions represented by the following equations:

$$B_4C + 6Cl_2 \rightarrow 4BCl_3 + C$$
$$B_2O_3 + 3C + 3Cl_2 \rightarrow 2BCl_3 + 3CO$$

The second key intermediate for preparing boranes, boron trifluoride (*3*), may be made directly from borax (*37*) or from boric acid (*41*) in accordance with the following equations:

$$Na_2B_4O_7 \cdot 10H_2O + 12HF \rightarrow Na_2\left[\begin{matrix} F_3B & & BF_3 \\ & O & \\ F_3B & & BF_3 \end{matrix}\right] + 16H_2O$$
$$Na_2O \cdot (BF_3)_4 + 3H_2SO_4 \rightarrow 4BF_3 + 2NaHSO_4 + H_2SO_4 \cdot H_2O$$
$$H_3BO_3 + 3HSO_3F \rightarrow BF_3 + 3H_2SO_4$$

The third key intermediate, sodium borohydride,

Figure 5. Open pit mine and refinery of United States Borax and Chemical Corporation, Boron, California.

may be prepared by the reaction of sodium hydride with trimethoxyborane (*30*):

$$4NaH + B(OCH_3)_3 \rightarrow NaBH_4 + 3NaOCH_3$$

Similar reactions for preparing sodium borohydride have recently been reported (*1*):

$$4Na + 2H_2 + BF_3 \rightarrow NaBH_4 + 3NaF$$
$$4Na + 2H_2 + NaBF_4 \rightarrow NaBH_4 + 4NaF$$
$$4Na + 2H_2 + B(OCH_3)_3 \rightarrow NaBH_4 + 3NaOCH_3$$
$$4Na + 2H_2 + 2B_2O_3 \rightarrow NaBH_4 + 3NaBO_2$$

Conversion of Key Intermediates to Diborane

The most efficient processes developed to date for the production of higher boranes are based upon the pyrolysis of diborane. As a consequence of this fact, diborane becomes the key borane in the synthesis of high energy fuels. It would be expected that diborane would result from the reaction of a boron-containing molecule with a molecule containing hydrogen. Usually the boron-containing material is one of the three key intermediates whose syntheses have been described above. Molecular hydrogen would be most desirable as the source of hydrogen. However, the reactions which involve molecular hydrogen have not given as high yields as desired and consequently the hydrogen is usually furnished by an active metal hydride.

In 1931, Schlesinger and Burg (*32*) prepared diborane (in poor yield) by the direct reaction of hydrogen with boron trichloride in a high voltage discharge:

$$2BCl_3 + 5H_2 \rightarrow B_2H_5Cl + 5HCl$$
$$6B_2H_5Cl \rightarrow 5B_2H_6 + 2BCl_3$$

In an effort to promote the reaction of hydrogen with boron trichloride more efficiently, Hurd (*18*) placed active metals in the heated reactor. The reaction is represented by the following equations:

$$3H_2 + 2Al \longrightarrow 2AlH_3$$
$$2AlH_3 + 2BCl_3 \longrightarrow B_2H_6 + 2AlCl_3$$
$$3H_2 + 2Al + 2BCl_3 \xrightarrow{200\text{–}400^\circ C} B_2H_6 + 2AlCl_3$$

Koster and Ziegler (*20*) modified this type of reaction (*a*) by the addition of ethylene to produce triethyl aluminum:

$$2Al + 3H_2 + 6C_2H_4 \rightarrow 2(C_2H_5)_3Al$$

and by (*b*) the utilization of boron trifluoride in place of the boron trichloride:

$$(C_2H_5)_3N \cdot BF_3 + (C_2H_5)_3Al \rightarrow (C_2H_5)_3N \cdot B(C_2H_5)_3 + AlF_3$$

The aluminum fluoride is recycled by treatment with boric oxide and sulfuric acid to make boron trifluoride which is used later in the process. The triethylamine adduct of the triethylborane reacts with hydrogen to give the triethylamine adduct of borane in accordance with the equation:

$$2(C_2H_5)_3N \cdot B(C_2H_5)_3 + 3H_2 \rightarrow 2(C_2H_5)_3N \cdot BH_3 + 6C_2H_6$$

The ethane liberated is dehydrogenated to ethylene for recycle to prepare triethylaluminum. The triethylamine adduct of borane is finally treated with a stronger acid, boron trifluoride, to liberate diborane and form the triethylamine adduct of boron trifluoride which is recycled as shown above:

$$2BF_3 + 2(C_2H_5)_3N \cdot BH_3 \rightarrow B_2H_6 + 2(C_2H_5)_3N \cdot BF_3$$

A classical method for the preparation of diborane was developed by Schlesinger and Brown (*29*) and involves the reaction of boron trifluoride etherate with lithium hydride, thus:

$$6LiH + 2BF_3 \cdot (C_2H_5)_2O \rightarrow B_2H_6 + 6LiF + 2(C_2H_5)_2O$$

Similar reactions involving active metal hydrides and boron trichloride are (*1*):

$$3Mg(BH_4)_2 + 2BCl_3 \rightarrow 4B_2H_6 + 3MgCl_2$$
$$3Ca(AlH_4)_2 + 8BCl_3 \rightarrow 4B_2H_6 + 6AlCl_3 + 3CaCl_2$$
$$3LiAlH_4 + 4BCl_3 \rightarrow 2B_2H_6 + 3AlCl_3 + 3LiCl$$
$$6LiH + 2BCl_3 \rightarrow B_2H_6 + 6LiCl$$

Diborane may be prepared from the third key intermediate, sodium borohydride, by allowing it to react with a Lewis acid or a protonic non-oxidizing acid. Typical Lewis acids which may be used are ferric chloride, cupric chloride and boron halides (*1*). A typical reaction with a protonic acid (*31*) is exemplified by the equation:

$$2NaBH_4 + 2HCl \rightarrow B_2H_6 + 2NaCl + 2H_2$$

Diborane may be obtained from active metal borohydrides by electrolysis, using a suitable electrode system and a suitable solvent such as di(methoxyethyl) ether (*1*). Many of the reactions for the generation of diborane from sodium borohydride are conducted in oxygenated solvents, such as the dialkyl ethers of polyalkeneglycols, alkyl ethers, tetrahydrofuran or dioxane. The first time a solvent is used the yields may not be as high as would be expected from the stoichiometry because of secondary reactions (*5*) such as represented by the equations:

$$2NaBH_4 + B_2H_6 \rightarrow 2Na(H_3B \cdot\cdot H \cdot\cdot BH_3)$$
$$2R_2O + B_2H_6 \rightarrow 2R_2O \cdot BH_3$$

Another route from an intermediate compound to a borane is concerned with the direct conversion of a metal boride to a higher borane in accordance with the unbalanced equation (*35*):

$$MgB_2 + HCl \rightarrow B_4H_{10} + B_5H_9 + B_6H_{10} + B_{10}H_{14} + MgCl_2$$

This is the classical reaction developed by Alfred Stock for the preparation of tetraborane.

Conversion of Diborane to Higher Boranes

As pointed out by Stock (*35*) many years ago, the known boranes may be classified into a B_nH_{n+4} series and a B_nH_{n+6} series, of which the B_nH_{n+4} series is the more stable:

B_nH_{n+4}	B_nH_{n+6}
B_2H_6	B_4H_{10}
B_5H_9	B_5H_{11}
B_6H_{10}	B_6H_{12}
B_8H_{12}	B_9H_{15}
$B_{10}H_{14}$	

These boranes are electron deficient molecules and considerable work has been undertaken to ascertain their structures (*2, 12, 13, 21, 22, 26*), their generation from diborane, and their subsequent interconversions (*4, 6, 10, 16, 23, 24*).

Although the mechanisms for the reactions resulting from the pyrolysis of diborane are not completely understood, it is known that the higher boranes are obtained from the pyrolysis of diborane. The mechanism by which these boranes are formed is controversial, but experimental evidence indicates that the unstable

tetraborane and pentaborane(11) are formed along with the stable pentaborane(9). There is evidence that pentaborane(11) can be converted to pentaborane(9) at low temperatures (*4*). It is believed that the interaction of these lower boranes give rise to the higher boranes. For example, with the use of boron,[10] Hillman, Mangold, and Norman (*16*) concluded that decaborane is formed by the interaction of diborane and pentaborane(9) in accordance with the stoichiometry of the equation:

$$2B_5H_9 + 5B_2H_6 \rightarrow 2B_{10}H_{14} + 10H_2$$

Thus in a high energy fuel process, higher boranes may be obtained by the pyrolysis of diborane under suitable conditions.

Alkylation of Boranes

As shown in Figure 4, a high energy fuel, such as an alkyl borane, may be prepared by alkylation of the key intermediates, alkylation of diborane, or alkylation of the higher boranes. As established in the alkylation of a hydrocarbon, alkylation of a borane will proceed more readily if a functional group, such as a halogen or an active metal atom, is attached to the borane. For example, a haloborane may react with a metal alkyl to produce an alkyl borane, or a metal polyhydropolyborate may react with an alkyl halide to produce an alkyl borane.

Equations for typical reactions for the preparation of haloboranes are (*28, 32, 35*):

$$B_2H_6 + Br_2 \longrightarrow B_2H_5Br + HBr$$

$$2B_2H_6 + 7HBr \xrightarrow[90°C.]{AlBr_3} B_2H_5Br + 2BBr_3 + 7H_2$$

$$5B_2H_6 + 2BCl_3 \longrightarrow 6B_2H_5Cl$$

$$B_{10}H_{14} + 2Br_2 \longrightarrow B_{10}H_{12}Br_2 + 2HBr$$

$$2B_{10}H_{14} + 3I_2 \xrightarrow{110°C.} B_{10}H_{13}I + B_{10}H_{12}I_2 + 3HI$$

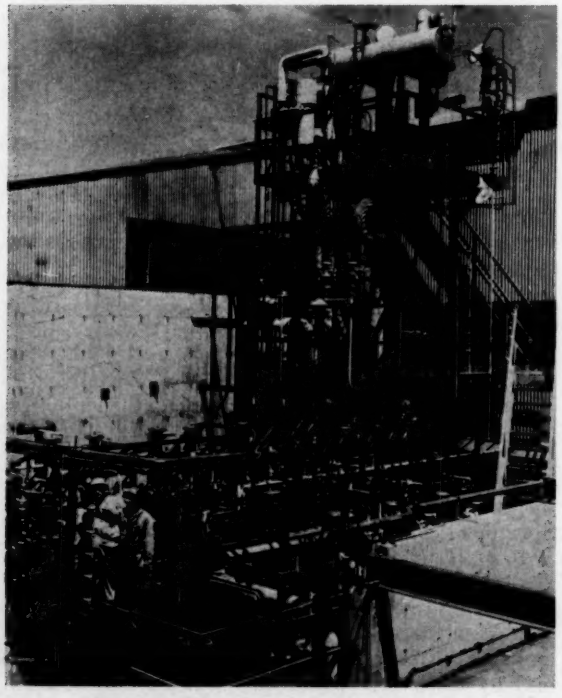


Figure 6. High energy fuel distillation area.

Metalloboranes may be prepared from metal amalgams in accordance with the following reactions (*35*):

$$B_2H_6 + NaHg_x \rightarrow Na_2B_2H_6 + Hg$$
$$B_4H_{10} + NaHg_x \rightarrow Na_2B_4H_{10} + Hg$$

Boranes may be alkylated or arylated with an unsaturated hydrocarbon (*17*):

$$B_2H_6 + 6RCH{=}CH_2 \rightarrow 2(RCH_2CH_2)_3B$$
$$B_2H_6 + 6C_6H_6 \rightarrow 2(C_6H_5)_3B + 6H_2$$

Alkoxy derivatives of boranes may be prepared by allowing a borane to react with an appropriate alcohol (*7*), thus:

$$B_2H_6 + 4CH_3OH \rightarrow 2(CH_3O)_2BH + 4H_2$$
$$B_2H_6 + 6CH_3OH \rightarrow 2(CH_3O)_3B + 6H_2$$

In addition to these methods for the alkylation of boranes, the Grignard reaction also may be employed. For example, decaborane will react with a methyl Grignard reagent in accordance with the following equations (*34*).

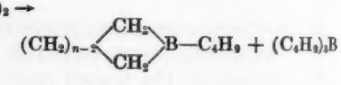
$$B_{10}H_{14} + CH_3MgI \rightarrow B_{10}H_{13}MgI + CH_4$$
$$B_{10}H_{13}MgI + 2C_6H_5CH_2Cl \rightarrow C_6H_5CH_2B_{10}H_{13} + C_6H_5CH_2I + MgCl_2$$

Borane derivatives will react with double Grignard reagents. For example, with chlorodibutylborane instead of producing bis(dibutylboranyl) alkane as expected:

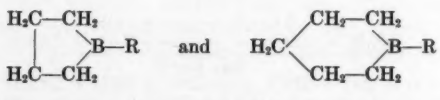
$$BrMg(CH_2)_nMgBr + 2(C_4H_9)_2BCl \rightarrow (C_4H_9)_2B(CH_2)_nB(C_4H_9) + 2MgBrCl$$

cyclization takes place to yield:

$$(C_4H_9)_2B(CH_2)_nB(C_4H_9)_2 \rightarrow$$



Rings such as



have been prepared in which R is a butyl or a phenyl group (*9, 38*).

High energy fuels under the trade names of HEF (Olin Mathieson Chemical Corporation) and Hi-Cal (Callery Chemical Company) are currently being produced in plants owned by these companies and in plants operated by these companies for the Department of the Air Force and the Department of the Navy. The Callery Chemical Company has a company owned plant at Lawrence, Kansas, and a plant operated for the Department of the Navy at Muskogee, Oklahoma. The Olin Mathieson Chemical Corporation has a company owned plant, a plant operated for the Department of the Navy, and a plant operated for the Department of the Air Force, all at Niagara Falls, New York (Fig. 6).

Properties of High Energy Fuels

The pertinent properties of an HEF fuel are compared with JP-6 in Table 3 (*15*).

The table indicates that the borane fuels have heats of combustion which are much superior to that of JP-6. Also, the specific gravity of the high energy fuels is slightly higher than that of JP-6; therefore,

Table 3. Comparison of JP-6 and HEF

	JP-6	HEF
Heating value, Btu/lb	18,600	>25,000
Specific gravity at 70°F	0.78	0.82
Flame speed	X	6–10X
Chemically stable at °F	500	500

some of the properties which are related to being able to fly farther have been improved. Of interest also is the fact that the flame speed of the HEF fuels is approximately six to ten times faster than that of the JP fuel, thus improving the properties of the fuel for high altitude flying. The table also indicates that the HEF fuels have matched the JP fuels with regard to resistance to thermal decomposition at elevated temperatures.

As stated previously, one of the objectives of the research program to develop a high energy fuel was to make it possible for the jet planes and missiles to go farther. The distance that a plane may go may be calculated from the basic range equation:

$$R = N_0 H \frac{L}{D} \log \left(1 + \frac{dv}{W}\right)$$

in which R is the range, N_0 is the over-all efficiency of the propulsion system, H is the mass heating value, L/D is the lift-drag ratio, d and v are the density and volume of the fuel, respectively, and W is the weight of the aircraft without fuel. This equation shows the dependence of range upon the fuel properties, heat of combustion, H, and the density of the fuel, d. Assuming that all of the other terms in the equation remain essentially constant, it is clear that if the heat of combustion of the high energy fuel is 50% greater than that of a JP fuel, the range will be 50% greater. The range of a missile is proportional to the thrust of the rocket engine, which is commonly expressed as specific impulse. A simplified equation for specific impulse is:

$$I_s = (\Delta H/\overline{M})^{1/2}$$

in which I_s is the approximate specific impulse in pounds of thrust per second per pound of propellant, ΔH is the molar heat of reaction of the propellant, and $\overline{M}$ is the average molecular weight of the exhaust gases.

The performance which could be expected of a borane fuel is compared with the performance of JP-4 in Figure 7 (*25*). The curve represents the mass ratio of a missile, R, expressed as the weight of the vehicle at take off, W_{to}, divided by the weight of the vehicle at burn out, W_{bo}. In the figure, assuming R is equal to 2, JP-4 and liquid oxygen having a specific impulse of approximately 272 seconds at 600 psi chamber pressure would propel a vehicle approximately 210 miles. Substituting liquid diborane for JP-4 as the fuel, and using liquid oxygen as the oxidizer, the resulting propellant having a specific impulse of approximately 340 seconds would propel the same vehicle approximately 50% farther, or about 315 miles. Thus in the above discussion it is shown that HEF fuels increase the range of air breathing engines or rocket engines by about 50% over that which may be obtained with a JP fuel in the same vehicle.

Boranes as fuels compare favorably with other well established fuels when incorporated into propellants as shown in Table 4.

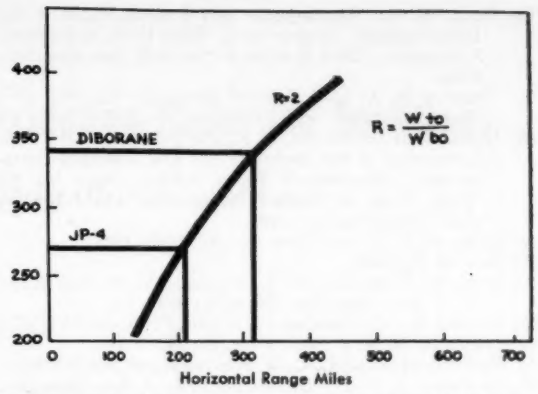


Figure 7. JP-4 and liquid oxygen. Liquid diborane and liquid oxygen.

Table 4

Propellant	Wt. % free H_2	I_s sec (20 atm)
N_2H_4–F_2	0	279
N_2H_4–F_2–H_2	10	323
O_2–H_2	16	354
F_2–H_2	8	361
B_2H_6–O_2–H_2	12	363
B_5H_9–O_2–H_2	14	363

Table 4 (*8*) indicates the advantage of using hydrogen as a fuel in propellants. When only 10% of hydrogen is added to the hydrazine-fluorine system, the thrust, expressed as specific impulse, is increased by approximately 15%. Without the hydrazine, the hydrogen-fluorine system gives a further increase in specific impulse of approximately 12%. However, it is to be noted that the propellants containing boranes have higher specific impulse values than are available from such well-known energetic systems as the oxygen-hydrogen and fluorine-hydrogen systems.

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E. W. Balson
The University
Southampton, England

Apparatus for the Study of Liquid-Vapor Equilibria

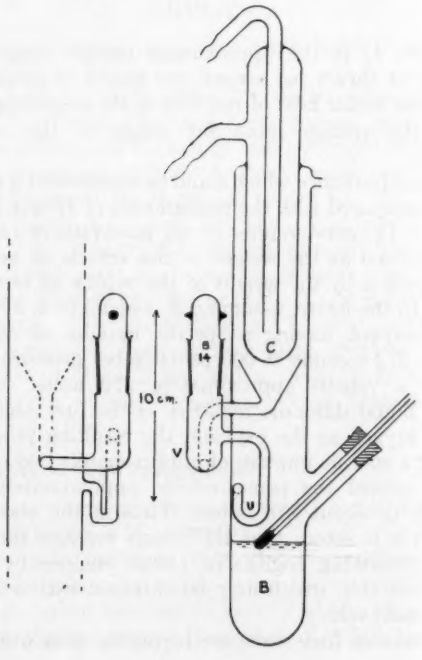
Among the many types of still used for the investigation of liquid-vapor equilibria are several of simple design which are suitable for student use, such as that described by Choppin, *et al.* (J. CHEM. EDUC., **24**, 491 (1947)) and the very simple form mentioned in "Experimental Physical Chemistry" (DANIELS, MATTHEWS, WILLIAMS, ET AL., 5th ed., McGraw-Hill Book Co., **1956**, p. 77).

Another compact type of still which has been used successfully by undergraduates in the physical chemistry laboratory at this university is described below.

The apparatus is shown in the diagram, to scale, and is constructed in Pyrex glass. The liquid (*ca.* 50 ml) is boiled in *B*, and condenses on the water-cooled thimble *C* and flows to the side vessel *V* by way of the funnel *F*, the overflow from *V* returning to boiler *B* through the U-tube *U*. A 0–50° or 50–100° thermometer, graduated to 0.1°, is fitted into the side arm as shown.

In use, equilibrium is attained in 5 to 10 minutes and is indicated by constancy in composition of the condensate in *V*, both this composition, and that of the liquid in the boiler being determined from their respective refractive indices. Benzene-acetone, benzene-methyl alcohol, and chloroform-methyl alcohol mixtures have been employed.

Despite their somewhat fragile appearance, one of the two constructed four years ago has survived; the other required repair recently. Possibly compactness has some influence on the life of the apparatus when used and stored by students.



Richard G. Yalman
Antioch College
Yellow Springs, Ohio

Writing Oxidation-Reduction Equations

A review of textbook methods

One of the problems facing the general chemistry instructor is to teach students to write oxidation-reduction equations. Although there has been considerable discussion of the merits and meaning of various methods in the pages of THIS JOURNAL, the method learned and used by the student is somewhat dependent upon the instructor's choice of text. Many new general chemistry books have been written during the past decade and most of the older books have now been revised. All of these books contain excellent material on electrochemistry and elements with variable oxidation states. However, the contents of this material do not necessarily include directions to the student which will aid him in writing oxidation-reduction reactions. The purpose of this paper is to review those parts of a number of textbooks which do contain aids or suggestions which will help the student to balance oxidation-reduction reactions.

The suggestions may be confined to a single chapter appropriately entitled "Oxidation-Reduction" (*4, 7, 9, 11, 13*). When the techniques of writing equations are included with other material, the chapter headings are generally composite. Typical titles are "Hydrogen Peroxide and Oxidations in General," (*12*) "Hydrogen, Reduction-Oxidation, Oxidation States" (*6*), "Chlorine and Hydrochloric acid; the Oxidation State" (*8*) and "Oxidation-Reduction, Half Reactions, Galvanic Cells." Sometimes there is no hint from the chapter heading that material on how to write equations is included. Thus in the book by Sorum (*19*) detailed instructions for balancing ionic reactions are found in Chapter 16 which is simply called "The Halogens." Finally a number of authors (*6, 8, 9, 17*) present the oxidation-number and the ion-electron methods for balancing equations in two (or more) separate chapters.

General Advice to the Student

Using bold-face type, Pauling (*11*) writes "BE SURE THAT YOU KNOW WHAT THE REACTANTS ARE AND WHAT THE PRODUCTS ARE." Mack, *et al.* (*8*) write nearly the identical sentence in italics. A similar emphasis on *knowing* what the reactants and products will be or on *knowing* what the oxidation numbers and characteristic compounds the elements are capable of assuming is made by several others (*5, 9, 12*). Often the writer then (*3, 4, 5, 11*) goes on to point out that the reactants and products can be determined from a knowledge of their chemical characteristics, by direct examination and analysis, by examining the literature, and by the use of chemical theory.

Only two authors give definite rules for the determination of the products of oxidation and reduction. Schlesinger (*14*) writes:

> (1) The more concentrated the solution of the oxidizing agent, the smaller will be the change in its valence number. . . .
> (2) The stronger the reducing agent, the greater the change in the valence number of the oxidizing agent.

Hopkins and Bailar (*5*) give completely different rules:

> (1) We should not expect an active metal to be produced by the reduction of its ions in the presence of water.
> (2) We should not expect the oxide of a metal to be produced in a reaction if the acid is present. Similarly the oxide of a nonmetal will not be produced in the presence of an hydroxide-base, such as NaOH.

On the other hand Cragg and Graham (*3*) state that "there is no 'rule' for ascertaining what are the products of a particular reaction." and Timm (*21*) writes " . . . do not be concerned if you cannot predict what the products of a certain reaction will be."

Definition of a Chemical Equation

Few authors include a formal definition of an equation. The clearest definition is in the book by Sisler, *et al.* (*17*): "a correct equation must . . . represent the quantitative relationships involved in the reaction. . . ." They go on to say that "in the light of the Law of the Conservation of Mass and of the atomic theory, . . . there will be the same number of atoms of each element in the products . . . as there were in the reactants." Several other authors (*8, 14, 15*) refer to the concept of conservation of mass while some (*11, 16, 18*) refer to the conservation of both mass and charges. The conservation of electrons, rather than charges alone, is mentioned in two books (*12, 20*). For example, Rochow and Wilson (*12*) state that "no electrons are created or destroyed." However, none of the authors point out that electrons have mass and therefore when one conserves mass, the number of electrons, charges, etc., are automatically conserved.

In one way or another all of the other authors also refer to the *balancing* of the numbers of atoms, charges, oxidation states, and/or electrons. Again, it is Cragg and Graham (*3*) who point out that "Strictly speaking, every formulation of a reaction that is truly the reaction . . . is already balanced." And the only text which interprets the symbolism of an equation for the student is the one by Nebergall and Schmidt (*9*). They point out that the arrow (or equal sign) is read as "gives," "produces," "yields," or "forms"; that the + sign between the formulas for two reactants on the left side implies "reacts with" while on the right it does not mean arithmetical addition, but "and."

Definition and Assignment of Oxidation States

Every book examined used the term oxidation and/or valence state. In many the two terms are used synonymously while one (*10*) used the term valence exclusively. The oxidation state may be defined as the charge on the ion, whether simple or complex (*17*), the number of electrons lost (and gained) (*12*), or the number of electrons an atom uses in sharing electrons with other atoms (*2*). Many authors either directly (*3, 5, 8, 9, 10, 14, 15, 16, 18*) or indirectly (*5*) try to define oxidation state on a theoretical or physical basis and make use of the concept of electronegativity. Thus a typical definition of oxidation state (or number) is "the charge which an atom appears to have when the electrons . . . shared between two unlike atoms are counted with the more electronegative atom" (*16*).

The difficulties in using the concept of electronegativity to define oxidation states is emphasized by the occurrence of fractional oxidation states. In spite of their discussion in THIS JOURNAL,[1] Sisler, VanderWerf, and Davidson (*17*) do not mention them in their text. In fact only Seinko and Plane (*16*) and Hildebrand and Powell (*4*) discuss fractional oxidation states (both include $+2^1/_2$ sulfur in tetrathionate). Hildebrand and Powell (*4*) conclude with the statement that "the oxidation numbers do not need to be theoretically correct . . ., they need only to be arithmetically consistent."

The inadequacies of a theoretical basis for defining the oxidation state of an element are recognized by many other authors (*2, 11, 13, 16, 20, 21*) who point out that the actual assignment of oxidation states is both arbitrary and a matter of convenience.

More often, however, the authors try to relate the arbitrary assignment of oxidation states to a theory. Typical is the statement from Hopkins and Bailar (*5*) "In carbon dioxide . . . oxygen is the more negative element, so we count carbon as +4 and oxygen as −2." This same mixture of theory and convenience may be found in the rules which are often given to aid the student in assigning oxidation states. Thus in the book by Timm (*21*) rule 4 reads " . . . the oxidation number of the more electronegative element is negative and of the less electronegative element positive." This is followed by subrule 4*a* "The oxidation number of oxygen is always −2." Even when the rules are completely arbitrary, there is an attempt to make them logical. For example, the first three rules in the book by Rochow and Wilson (*12*) are:

(1) All elementary substances . . . have an oxidation number of zero.

(2) The algebraic sum of the oxidation numbers of all the atoms of any neutral compound must be zero. In any ion the algebraic sum must equal the charge on the ion.

(3) It follows that oxygen in all compounds but peroxides has an oxidation number of −2.

At some point in their discussion the remaining authors also assign to oxygen an oxidation state of −2 (except in peroxides), a procedure first introduced by Johnson over 75 years ago.[2] In practice both the student and instructor undoubtedly ignore the gain or loss of electrons, electron shifts, electronegativities, and other terms or concepts. Instead they will remember and apply the "Johnson Rule." Nevertheless there may be some value in the attempt to correlate oxidation-reduction in complex material with bonding concepts, particularly since such concepts are again used to explain the reactions of organic compounds.

Definition of Oxidation

A number of texts (*5, 6, 7, 11, 13, 18, 19, 21*) point out that historically oxidation referred to the reaction of an element with oxygen itself. In addition all of the writers define oxidation either as a change in the oxidation state (*14, 16, 18, 19*), as the loss of electrons (*4, 5, 7, 8, 11, 12*) or as both.

The definitions for oxidation are complicated by several factors. In the first place when more than one definition is given, they are often given in widely separated portions of the text without reference to one another. For example, Sisler, VanderWerf, and Davidson (*17*) define oxidation in terms of oxidation state in Chapter XII and in terms of electron transfer in Chapter XXIV. Second, when oxidation is defined in terms of a change in oxidation state, the electron transfer definition may also be implied. This is because many authors define the oxidation state in terms of electronegativities and electron shifts. Finally the definition of oxidation by changes in oxidation state is complicated by attempts to give a student a physical picture of the process of oxidation. Thus Hopkins and Bailar (*5*) explain the change in oxidation state of carbon when methane is burned to form carbon dioxide by writing " . . . This does not mean that the carbon atom has *lost* eight electrons, it has lost the major control over eight electrons . . ." And Laubengayer (*6*) writes that in oxidation "Each electron that is lost or that becomes *less* associated with one atom must be gained or become more associated with another atom."

Methods of Writing Equations

Only Steiner and Campbell use the algebraic method first suggested by Bottomley.[3] In their first discussion of chemical arithmetic these authors use the inequality sign and indicate that the reaction may be balanced by using the coefficients x, y, and z. However, they do not pursue this method to the extent suggested by Bennett.[4]

Generally, various names, such as electron shift (*13*), valence change (*10*), "partial equations" (*20*), etc., are used to describe the methods of balancing oxidation-reduction reactions. Those most commonly used are "oxidation-number" and "ion-electron." In its simplest (or purest) form, i.e., without reference to electron shifts or electron gains or losses, the oxidation number method can be used to balance ionic (*4, 6, 9, 18, 19*) as well as molecular reactions (*6, 8, 12, 17, 19*). The ion-electron method was used without reference to oxidation states in nine books (*4, 7, 8, 9, 10, 16, 17, 18, 21*) and it was used without being named in four more (*1, 12, 15, 20*). There was only one book (*14*) which made no reference to the use of electrons in writing oxidation-reduction equations.

[1] VANDERWERF, C. A., DAVIDSON, W. A., AND SISLER, H. H., J. CHEM. EDUC., **22**, 450 (1945).

[2] JOHNSON, O. C., *Chem. News*, **42**, 51 (1880).

[3] BOTTOMLEY, J., *Chem. News*, **37**, 110 (1878).

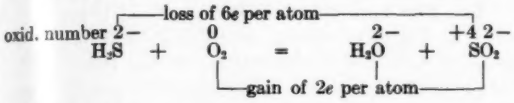
[4] BENNETT, G. W., J. CHEM. EDUC., **31**, 324 (1954).

Many books combined both methods of writing equations. The following examples are typical. Under the heading "Balancing Oxidation-Reduction Equations using Oxidation Numbers," Luder, Vernon, and Zuffanti (*7*) write:

(1) *Calculate all oxidation numbers assuming the oxidation numbers of oxygen and hydrogen to be −2 and 1, respectively.*
(2) *Make the number of electrons gained by the oxidizing agent equal to the number lost by the reducing agent.*

Similarly, Scarlett and Gomez-Ibanez (*13*) write "Manganese in the MnO_4^- is in the +7 oxidation state so the gain and loss of electrons. . . ." They also use half-reactions to illustrate the oxidation-number or, as they call it, the "electron shift" method.

Like many others, Steiner and Campbell use a diagram:



Two authors (*14*, *16*) use arrows pointing upwards to indicate a gain of electrons and arrows pointing downwards to indicate a loss of electrons while a third (*9*) uses arrows pointing in the opposite directions. In one book (*12*) the oxidation number method was introduced with the use of electron transfer. Yet in a review of the oxidation-number method in the appendix of this same book there was no mention of electrons.

Sometimes there is very little difference between the oxidation-number and ion-electron methods. For example, in the section on oxidation-number method Sienko and Plane (*16*) give the following rules:

(1) Balance electron transfer.
(2) Balance the net charge by placing H where required in order to maintain net charge balance.
(3) Place H_2O where it is required to balance the oxygen.

Later in a section on the ion-electron method these authors use the same rules, but in reverse order. And Hildebrand and Powell (*4*) give the same rules for the ion-electron method that Sienko and Plane (*16*) give for the oxidation-number method.

Hydrogen and Oxygen Balance

Although nearly all authors include rules for the hydrogen and oxygen balance, few offer an explanation for the use of these rules nor do they consider the differences between acidic and basic solutions. Often the student is told that "a *reasonable* way of balancing oxygen atoms would be to use water" (*7*) or that "oxygen atoms presumably appear as . . . water" (*14*) or that "H atoms must appear in H_2O" (*17*). In other books the student is reminded that since water and its ions are always present, they "may be used at will as reagents" (*8*), and that they may also be products (*11*).

Pauling (*11*) points out that hydroxide ion can exist in only extremely low concentrations in acidic solutions while Sienko and Plane (*16*) write that hydrogen ions do not exist in basic solutions. Sorum (*19*) discusses in detail the possible use of hydroxyl ion and hydrogen ion in acidic and basic solutions, respectively, and then he discusses why this cannot be done. On the other hand Sneed, Maynard, and Brasted (*18*) recommend that the hydrogen balance is first completed by the addition of hydrogen ions and then if necessary add hydroxyl ions to balance the charges. Their rules are quite complicated. Thus under the heading of balancing equations by the ion-electron method Rule III reads: "(*a*) balance the oxygen atoms by the addition of the necessary number of water molecules and the hydrogen atoms by the addition of the necessary number of hydrogen ions to the appropriate side of the arrow in each partial equation. III (*b*) *is applied only if the reaction takes place in alkaline solution* (*b*) if the reaction takes place in basic medium, perform step III (*a*) and then add to each side of the partial equation as many basic ions (as OH^- or CO_3^{--}) as are needed. . . ."

These rules are then applied to the chromite-chromate half-reaction.

There are also many comments or suggestions which occur in individual books. Of these the following are of general importance. Parks and Steinbach (*10*) are the only authors who explicitly state that oxidation-reduction reactions can take place in neutral solutions. Timm (*21*) points out that "it would have been improper to (use) free hydrogen as a product since none is liberated." Sisler, VanderWerf, and Davidson (*17*), in discussing the reduction of permanganate, write " . . . the permanganate and hydrogen ions are reduced to manganous ion and water." It is not clear whether this sentence is a mistake or whether these authors intended to emphasize the fact that the entire half-reaction is involved in oxidation-reduction. Sisler, VanderWerf, and Davidson have discussed the role of the hydrogen ion in the reduction of oxy-ions in THIS JOURNAL.[1] None of the authors mention, however, that the oxide ion, which is so strong a base that it would immediately react with a proton donor, is neither a reactant nor a product.

After reviewing 21 books, it is apparent that there are at least 22 different ways of presenting material on balancing oxidation-reduction reactions. In view of the demonstrated success of each of the authors as teachers, it is equally apparent that no one way is the correct or best way. Rather each instructor uses the method, or methods, or combination of methods with which he is most familiar. The fact that there are so many ways of accomplishing the same task may indicate that there is still a good deal of art in chemistry. And like art perhaps the technique of writing chemical equation reactions is best learned by constant repetition. Thus material on writing oxidation-reduction equations is introduced with the earliest section on chemical arithmetic. It is repeated in the chapters on oxygen and oxidation by oxygen, chemical nomenclature and oxidation state, bonding and electronegativities, electrochemistry and electrode reactions, and again in the descriptive chapters on the chemistry of elements with variable oxidation states. There is a suggestion by many that oxidation-reduction is related to acidity and basicity. Perhaps it might be worthwhile to emphasize the fact that equations involving oxy-ions are applications of the Brønsted-Lowry acid-base theory and chemical equilibrium.

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S. A. Greenberg[1]
Seton Hall University
South Orange, New Jersey

The Chemistry of Silicic Acid

Although a great deal of information on this chemistry has been reported in the last five years (*1*), many incorrect older concepts still appear in the current literature, in freshman textbooks, and in treatises on inorganic chemistry. Frequent references are made to the theoretical, but not to the actual existence of silicic acid H_4SiO_4, to the composition of silicic acid as H_2SiO_3, to the preparation of solutions of dimers or trimers of silicic acid, and to many other aspects of the chemistry of the acid for which no definite evidence has been advanced. In the present paper the currently accepted approach to the chemistry is reviewed for those who must present a clear picture to students and are not in this field of chemistry.

The element silicon contains four outer electrons, $3s^23p^2$. When the element shows a coordination number of four, these electrons form $3sp^3$ hybrid bonds (*2*). Because in $SiF_6^=$, SiP_2O_7 and in compounds with organic groups, silicon is octahedrally coordinated by six atoms (*3*, *4*, *5*), $3sp^3d^2$ hybridization has been suggested (*2*). However, recent Raman studies (*6*) are interpreted to indicate that monosilicic acid in solution exists as $Si(OH)_4$ rather than $H_2Si(OH)_6$.

An analysis of solubility (*7*) and emf measurements (*8*) has demonstrated that the acid is dibasic and dissociates in two steps

$$Si(OH)_4 + H_2O = SiO(OH)_3^- + H_3O^+ \quad pK_1 = 9.8(20°) \quad (1)$$

$$SiO(OH)_3^- + H_2O = SiO_2(OH)_2^= + H_3O^+ \quad pK_2 = 11.8(20°) \quad (2)$$

[1] Present address: Portland Cement Association, Skokie, Ill.

The pK values, however, are not sufficiently different to cause two breaks in the acid-base titration curve (Fig. 1). The monomeric species (H_4SiO_4, $H_3SiO_4^-$, and $H_2SiO_4^=$) are found only in solution and in the vapor phase. When the solutions are evaporated,

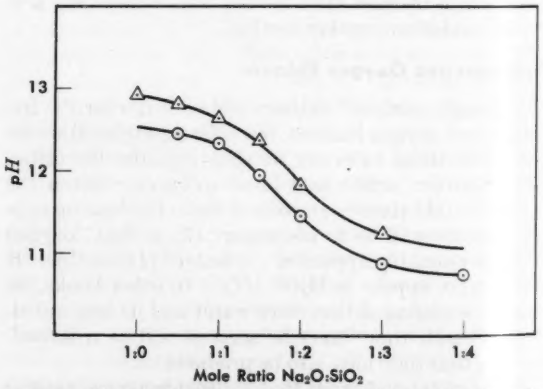

Figure 1. Neutralization curves of 0.1 *N* sodium hydroxide solutions by silica at 20° (Δ) (*9*) and 25° (0) (*10*).

silica gels form. Several methods for the preparation of monosilicic acid have been reported.

(1) Dilute solutions of sodium silicate above pH 11 contain monomeric silicic acid and its ions (*11*).

(2) Aqueous solutions in contact with solid silica

are saturated with the undissociated acid $Si(OH)_4$ and its ions (*1, 7, 8*).

(3) Monosilicic acid solutions have been prepared by hydrolyzing silicon tetrachloride or orthosilicic acid esters in aqueous solutions at low *p*H and at low temperatures (*1*).

(4) Solid silicates in which none of the four oxygens of the SiO_4 tetrahedron is shared by silicon atoms are reported to form monomeric acid solutions in water maintained at *p*H 3 with HCl (*1, 12*).

(5) When noncolloidal solutions of sodium silicate at 0° and *p*H 3 are passed through cation exchange resins in hydrogen form, monomeric solutions are produced (*1*).

(6) Brady (*13*) has discussed the presence of orthosilicic acid as a volatile species in steam at pressures above a few atmospheres.

Monosilicic acid $Si(OH)_4$ is the fundamental monomeric unit in polymeric glass, silica gels, crystalline silicas, and silicate structures (*14*). However, in the orthosilicates the oxygens of the SiO_4 tetrahedra are not shared in siloxane Si—O—Si bonds. Also in hydrated calcium silicates it has been proposed that hydroxyl bonds hold the tetrahedra together (*15*). Cummins and Miller (*12*) reported that the silica in calcium silicate hydrate disperses in acidic solutions, in which the rate of condensation reactions is slow (*16, 17*). It would be useful to an understanding of the silicate structures to know what the molecular weight of the silicic acid is.

Silica dissolves in water according to the equation derived by O'Connor and Greenberg (*18*)

$$\frac{dC}{dt} = k_1 S - k_2 CS \qquad (3)$$

where C is the concentration of monosilicic acid, S is the surface area, k_1 is the rate constant for solution or depolymerization, and k_2 is the rate constant for polymerization in neutral solutions. The surface area is proportional to the two-thirds power of the concentration. In alkaline solutions since the polymerization rate is low, k_2C may be neglected. Therefore, the rate of solution is proportional to surface area or to the *available* Si—O—Si bonds on the surface and the rate of polymerization to the concentration of monomeric species as well as the surface area.

The formation of polysilicic acid polymers such as silica gel, quartz, and silicates in alkaline solutions is believed to proceed by condensation reactions between silanol groups (*16, 19, 20*).

$$2\text{—SiOH} = \text{—SiOSi—} + H_2O \qquad (4)$$

or between monomeric and polymeric silicate ions —SiO^- and silanol groups.

$$\text{—SiO}^- + \text{HOSi—} = \text{—SiOSi—} + OH^- \qquad (5)$$

The kinetics for polymerization in alkaline solution has been represented by (*17*).

$$\frac{dC_{SiOH}}{dt} = k_1 \frac{C_{SiOH}}{C_{OH}} \qquad (6)$$

where k_1 is the rate constant and C_{SiOH} is the concentration of silanol groups.

The polymerization of silicic acid in acid solutions has been reported to proceed by different mechanisms (*21*). Alexander has demonstrated that below *p*H 3.2 at 1.90° the reaction is third order and above this *p*H value the reaction is second order. The details of the mechanisms are not too well understood.

The thermodynamic functions have been calculated for the equation (*22*).

$$SiO_2(s) + H_2O(l) = Si(OH)_4\ aq \qquad (7)$$

In this equation it may be seen that solid silica is in equilibrium with saturated solutions of silicic acid and the equilibrium constant K is equal to the activity of monosilicic acid. Several conclusions were drawn from the solubility results.

(1) The free energy states of colloidal silica and quartz are sufficiently different (1.32 kcal/mole) to result in an appreciable solubility (0.012%) at 25° for the amorphous silica and a small solubility for quartz (0.003%).

(2) There is a negative entropy change (ΔS = −28 eu) for colloidal silica dissolving in water which demonstrates the strong interaction between silicic acid and water (*22*). Several authors (*1*) have proposed that tetrahedral silicic acid and water have the same oxide structures. In one case the small silicon atoms fill the spaces and in the latter case the small protons are present.

(3) The equilibrium data show that only monosilicic acid exists in neutral solutions (*1*).

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Georg Lockemann
Mühle Hollenstedt über Northeim
Hannover
Translated by **Ralph E. Oesper**
University of Cincinnati
Cincinnati, Ohio

The Varieties of Scientific Discovery

In his "Aphorisms" the Goettingen physicist Georg Christoph Lichtenberg (1742–1799) states: "It is strange that only extraordinary men make the discoveries, which later appear so easy and simple." In fact, the greatest discoveries and inventions are no longer regarded as wonderful and astounding after they are known for a time; daily contact makes them appear quite natural and a matter of course.

Attempts have been made to divide the most important discoveries into groups, under the headings: chance, assiduity, genius. However, close examination soon reveals that none of these features can alone bring about a discovery. All three are always involved, though admittedly one or the other may predominate. Even the most favorable chance will be of no avail if it does not come to the proper observer who is capable of drawing the right conclusions from what he has seen. As Goethe astutely remarked (Faust, Part II):

> How Fortune linkéd is with Merit
> To their fool's wits doth ne'er occur,
> Had they the Philosopher's Stone, I swear it,
> The Stone had no Philosopher.

Diligent strenuous labor is required in every case before the searching investigator can clarify and make understandable the essence of the unhoped-for, the unexpected gift, which Fortune in a favorable mood has tossed into his lap. Also, in some cases, it is necessary even to overthrow opinions and "laws" which until then had been accepted as irrefutable axioms. In all cases, therefore, the third factor "genius" is the most important; without it the discovery could not have occurred at all. If this intellectual power is absent, all chance observations are nothing, all labor and diligence are in vain. Accordingly, every advance in the understanding of nature, in the conquest of natural forces and the resultant further development of culture and civilization are primarily dependent on the occurrence of unusually endowed investigators, the so-called men of genius.

Since the results of scientific researches are published in periodicals and books which are readily available to trained readers, the development of the sciences may be compared to a drama presented on a stage. In general the performance involves competent "actors" who appear and play their parts well in that they advance the knowledge of nature by their research contributions. But at times difficulties arise in the further development of the action, and the intervention of a "heroic character" becomes a necessity. Now it becomes a question whether the unseen director will give the proper cue, or whether the appointed character already is standing in the wings and can appear on the stage at the crucial moment. The history of science reveals that this actually takes place in many instances; in fact sometimes not merely one actor waits in the wings for the cue but rather two or three walk on to the stage at the same time. Indeed, there sometimes are premature actors, who in brilliant fashion foresee far in advance the coming difficulties or crises in the action; impatient, they do not wait for the cue but to the consternation of the other actors appear in their midst ahead of time and are pushed aside as unwanted noncomforming interlopers. Not until much later do the other actors and the audience realize that these unwelcomed persons had sensed the correct thing much in advance and had meant well. Sometimes this realization comes only after they themselves have departed from the scene.

However, there is a third class of discoverers who, totally unconcerned about the unfolding of the plot, make a discovery which at first is completely inexplicable, and with this they jump quite unexpectedly into the midst of the peaceful proceedings. They demolish all doubts of the correctness of their discovery by the sheer weight of the experimental evidence in that at the same time they create a new line of research which until then had been looked on as impossible.

Well-Timed Discoveries

Timely discoveries are made when the whole trend of development of the scientific investigation is in their direction. Conjectured and awaited, they are "in the air" and the great man who makes them appears opportunely. Among the many examples that may be cited are rather many in which more than one person made the discovery at almost the same time. Though this may be beneficial to the science itself, it often proves painful for the individual investigators concerned. Such essentially simultaneous discoveries usually give rise to the unpleasant and highly publicized priority disputes. Each of the happy discoverers is of the opinion—and rightly so—that the great discovery is his alone and he defends his claim with all his might. The pure joy of the discovery is soon sullied when he finds that he must spend much time and energy in upholding his rights; the disputes forced upon him rob him of his peace of mind, and this without any benefit whatever to science.

The following example selected from among the many instances of discoveries made independently by

The more lengthy German text of this paper appeared in *Naturwissenschaftliche Rundschau*, June 1957, pp. 219–24. The publishers have kindly authorized the present translation.

two or even more individuals will illustrate such occurrences and their correlative features:

The science of mathematics, confined to analytical methods, had reached its limits in the second half of the seventeenth century. There was a glaring need for a new procedure for solving problems that were obviously beyond the capabilities of the known systems of calculation. In close succession, two great minds came forward with new ideas presenting the same basic thoughts in a somewhat divergent form. They were: the Englishman Isaac Newton (1643–1727) with his method of fluxions, and the German Gottfried Wilhelm Leibniz (1646–1716) with his differential and integral calculus. Though they had arrived at the brilliant end-result independently, their lives henceforth were embittered by priority disputes, largely forced on them by their embattled partisans, who of course were men of far lower stature.

A similar controversy involving priority arose a century and a half later with respect to the discovery of the principle of the conservation of energy. The principals were Julius Robert Mayer (1814–1878) and Hermann Helmholtz (1821–1894). After rejection by Poggendorf, the editor of the *Annalen der Physik*, Mayer's "Remarks on the Forces of Inanimate Nature" was published by Liebig in 1842 in his *Annalen der Chemie und Pharmazie* but attracted no attention. Five years later, Helmholtz put out his treatise "On the Conservation of Energy" but would not acknowledge Mayer's priority. At this same time the highly educated English brewer James Prescott Joule (1818–1889) was making measurements of the mechanical equivalent of heat, and as early as 1837 the German chemist Carl Friedrich Mohr (1806–1879) had developed similar ideas without being able to come to a clear-cut decision on the matter.

Several similar instances should be mentioned at least briefly. Justus Liebig (1803–1873) and Jean Baptiste Dumas (1800–1884) contested the other's priority regarding the recognition of the natural cycle of materials (1840–41). The theory of the self-chaining of carbon atoms advanced as early as 1852 by the Austrian chemist Friedrich Rochleder (1819–1874) was again set forth (1857) almost simultaneously by the Scotchman Archibald Couper (1831–1892) and the German chemist August Kekulé (1829–1896), and through the concept of valence the structure theory of organic chemistry was founded at the same time. The hexagonal structure of benzene, developed in 1865 by Kekulé on the basis of a dream vision, proved so fruitful for the further development of the aromatic compounds that a "Benzene Celebration" was held in honor of its 25th anniversary, but it had already been proposed in 1861 by the Austrian chemist Joseph Loschmidt (1821–1895).

A striking example showing that not only discoveries but also inventions sometimes are "in the air" and that occasionally different scientists are working on the same problem unknown to each other is provided by the discovery of the method of preparing alizarin in the laboratory. The German chemists Carl Graebe (1841–1927) and Carl Liebermann (1842–1914) submitted their application for a patent for making this coloring matter of the ancient madder on June 25, 1869, whereas William Henry Perkin (1838–1907) applied for a patent in London covering the same process just one day later.

Other noted instances of the many discoveries that were announced at practically the same times include the formulation of the periodic system of the chemical elements by Lothar Meyer (1830–1895) and Dmitri Mendeleev (1834–1907) in 1869 and the founding of stereochemistry and the announcing of the theory of the asymmetric carbon atom in 1874 by the Hollander Jacobus Henricus van't Hoff (1852–1911) and the Frenchman Jules Achille le Bel (1847–1936).

Premature Discoveries

This group includes those discoveries that are made before the general state of scientific investigation affords the possibility of accepting them intelligently. The premature discoverers are ahead of their times, their findings are generally rejected, and they sometimes are even regarded as crackpots. Their speech is not understood by their contemporaries. What they themselves see clearly appears confused and obscure to others. Accordingly, they perhaps go through life misunderstood and they strive vainly to overcome the "resistance of the obtuse world."

A prime example of a chemist who was forgotten because his great discovery came too early was Jeremias Benjamin Richter (1762–1807) who by introducing mathematics into chemistry founded chemical stoichiometry and discovered the neutralization law. In his minor post as "arcanist" at the Royal Porcelain Works at Berlin he received no attention for his fundamental discoveries regarding the neutralization process and the constancy of combining ratios. His ideas were really appreciated only long after his death when they became dominant building blocks in the entire chemical science.

The young English scientist J. J. Waterston (1811–1883) suffered a similar tragic fate. In 1845 he submitted to the Royal Society a paper in which he developed his ideas on the gaseous state. It was quietly interred in the files as being of no consequence where it was accidently discovered 30 years later by Lord Kelvin. To the latter's amazement, he found that it contained the basic features of the kinetic theory of gases, which in the interim had been set up by the German physicists August Karl Krönig (1822–1879) and Rudolph Clausius (1822–1888) and which for a quarter of a century had already played a leading role in chemistry and physics. Inquiries were then instituted about Waterston and it was learned that overcome by despair he had gone to India and left no further trace.

The history of medicine likewise contains instances of unappreciated premature discoveries. The German-Hungarian physician Ignaz Semmelweis (1818–1865) while working in the maternity wards of the Viennese hospitals became well acquainted with childbed fever whose ravages were claiming more and more lives. He came to the opinion (1847) that the deadly poison was being carried from woman to woman by the physicians themselves on their dirty hands and instruments. Since it was well known that the odor arising from putrefying masses could be removed by chlorine, Semmelweis thought it might also be useful with suppurating cases. Accordingly he introduced the practice

of washing the hands and instruments with chloride of lime solution and had much success. However, this measure was rejected by most of the physicians, probably because he undiplomatically called those who did not adopt his procedure "murderers." The disdain which greeted his discovery and the treatment he himself received from some of his professional colleagues affected him so deeply that he was close to insanity for a time. Actually he was the discoverer of practical disinfection and after his death a monument was erected to his memory in Budapest carrying the inscription "The savior of mothers." Semmelweis' chlorine water had been practically forgotten when the English surgeon Joseph Lister (1827–1912) in 1867 introduced carbolic acid as disinfectant. It was more than a generation after Semmelweis that Robert Koch (1843–1910) in 1881 at Berlin laid down the scientific bases of disinfection and aseptic practices.

There are also instances of misunderstood premature discoveries which occurred without making any stir in the scientific world but in which the indifferent reception was accepted quietly by the discoverer with no apparent psychic or other effects. A typical instance is that of Gregor Mendel (1822–1884), the discoverer of the law of biological heredity. In the garden of the monastery at Brünn (now Brno) this Augustinian monk made systematic experiments on the crossing of various strains of plant hybrids and in 1865 came to a knowledge of the laws governing the transmission of certain characteristics, i.e., of regularities which have now been generally accepted under the name of Mendelian laws. However, he published his findings and conclusions in an obscure periodical, and these fundamental discoveries remained effectively concealed from the outside world. Consequently, it was possible for these same discoveries to be made again, "at the proper time" a generation later, in 1900, i.e., after botanical research had progressed sufficiently to handle and appreciate this problem properly. These later discoverers, who announced their results at approximately the same time, were: the German botanist Carl E. Correns (1864-1933), the Hollander Hugo de Vries (1848–1935), and the Austrian Erich von Tschermak (1871).

In this connection it is well to remember the rule: "He becomes the true discoverer who establishes the truth; and the sign of the truth is the general acceptance. . . . In science the credit goes to the man who convinces the world, not to the man to whom the idea first occurs." (Dubos, "The White Plague," 1952).

Unforeseen Discoveries

This group includes those discoveries which do not lie in the orderly course of scientific research, which are not made before the times are ready for them, and which cannot be anticipated or at most only in the wild phantasies of a Jules Verne. They fall entirely outside the usual bounds of strictly scientific investigations, and must be looked on as the fruit of unbridled ingenious notions except that by an appropriate experiment it is possible to confirm them to the satisfaction of even the most incredulous scoffers. Such unexpected glimpses into the "interior of nature" are granted but seldom to individual researchers and then in a singularly fortunate moment. The discovery is completely outside the accustomed limits of the line of study; it reveals characteristics and powers of nature which up till then had been held to be quite impossible. The investigator himself is so astounded by the unlooked-for discovery, is so dazzled by the blazing new light, that he requires a certain period of inner composure to convince himself that he is not the victim of self-deception. No competitors enter the picture. There is no opportunity for priority debates to arise. Those who are gifted with hindsight, who subsequently invariably claim to have known everything beforehand, must keep silent under these circumstances. Obviously a particularly important role is played by chance in these unanticipated discoveries.

The history of physics is the most fertile source of unlooked-for discoveries. Typical instances include the discovery of electromagnetism in 1820 by the Danish scientist Hans Christian Oerstedt (1777–1851) and that of the catalytic action of platinum in 1820 by the German chemist Johann Wolfgang Döbereiner (1787–1851). When the German chemist Robert Bunsen (1811–1899) and the German physicist Gustav Kirchhoff (1824–1884) were working together on the phenomena which became the basis of spectrum analysis, they grew so excited that the usually collected and grave Bunsen exclaimed "If the dark D-line actually appears in the spectrum, Kirchhoff, I believe I shall go crazy."

When, in 1896, Konrad Wilhelm Röntgen (1845-1923) first observed the penetrating power of the X-rays, he shut himself in his laboratory for days to prove to himself by intensive experimentation that he had not deceived himself. That this discovery had not previously come to the highly skilled physicist Philipp Lenard (1862–1947) who had previously done such outstanding work on cathode rays, was doubtless due to the absence of the necessary element, chance.

The eminent physical chemist, teacher, philosopher Wilhelm Ostwald (1853–1932) believed everything between heaven and earth can be expressed in a formalized understandable form. Among others, he developed a "good fortune formula" with which however he did not have much success either with his professional colleagues or others to whom he attempted to apply this mode of assessing real success and happiness. If, however, this concept of good fortune is applied to the various discoverers it will be found from what has been stated above, that the surprised discoverers were the happiest, the premature discoverers the least happy, while those whose discoveries were timely stand between because the joy in their discoveries is so often clouded by priority disputes.

The preceding text applies to actual discoveries and true discoverers, who in terms of the analogy to a drama being presented before the public really appear in the performance. There are also those who stay in the wings, or if they do appear their stay on the stage is only temporary. Accordingly, to the three positive groups of discoveries there should be added two negative groups, the discoveries that were missed and those that were imagined.

Missed Discoveries

A missed discovery is one that a scientist brushes by in the course of his studies without being aware of its

presence, or one which he fails to achieve because for some reason or other his investigation is broken off just as the imminent discovery is about to come to light. Obviously in all such cases this near-miss becomes apparent only after the actual discovery has been made by some one else. Even though the often-proposed *Journal of Futile Experiments* has never been published, the history of science discloses that the number of discoveries that have been allowed to slip through the fingers of various workers is extensive; perhaps it is the largest of all the groups. The classic example is found in the long antecedent history of the discovery of oxygen, which extends over about 250 years from the time of Leonardo da Vinci (1452–1519). To be sure, these investigators in the seventeenth century, like da Vinci himself, really should be placed in the category of premature discoverers.

The French physician Jean Rey (d.1645) and the English scientists Ralph Bathurst (1620–1704), Robert Hooke (1633–1703), and John Mayow (1645–1679) were on the track of the mysterious element but could not run it down. Free oxygen was generated for the first time by the Danish polyhistor Ole Borch (1620–1691) but he could not recognize it as such. Even after the pneumatic trough was devised in 1727 by Stephen Hales (1677–1761), an English rural clergyman, and thus provided the means of collecting individual gases separately, it was more than a half a century before oxygen was eventually actually "discovered." The Paris apothecary Pierre Bayen (1725–1787) furnished a model example of a missed discovery. He obtained a gas, which he referred to as *fluide elastique*, by heating red oxide of mercury, and when he heated metallic mercury in this gas it was again transformed into "mercurius praecipitatus per se." However, he did not recognize the true nature of the gas. Had he performed the simple experiment of inserting a glowing splint into the gas he could have laid claim to being an actual discoverer of oxygen. But since he omitted this crucial experiment, he was forced to concede this fame to the English cleric Joseph Priestley (1733–1804), who made the decisive experiment on August 1, 1774. However, it later became known that Priestley himself had been preceded in this discovery by the German-Swedish apothecary Carl Wilhelm Scheele (1742–1786) who a few years earlier (1771–72) had prepared "fire air." During this period of near discovery of oxygen, the phlogistic hypothesis, that had been set up by the Halle professor Georg Ernst Stahl (1660–1734) on the basis of the teachings of Johann Joachim Becher (1635–1682), had become so thoroughly entrenched that even the discoverers of oxygen, namely Priestley and Scheele, remained firm adherents of this hypothesis to the end of their days. The great theoretician Antoine Laurent Lavoisier (1743–1794) had to come on the scene to complete the discovery of oxygen, whose protracted discovery offers a true instance of a discovery-synthesis.

Since even the chemical Joves sometimes nod, it is not too surprising that both of the famed chemical friends, Liebig and Wöhler, experienced the chagrin of missing the *discovery of discoveries* in chemistry, i.e., the discovery of a new element. In 1826, Justus Liebig (1803–1873) then a young professor at Giessen, read with an emotion akin to shock that the French apothecary Antoine Jerome Balard (1802–1876) at Montpellier had discovered a new element in Mediterranean Sea water. This heavy red-brown liquid evolved vapors of the same color whose terrible odor led Gay-Lussac to suggest that the new element be named bromine from the Greek *bromos* (stench). The deeply affected Liebig arose, went to his collection of chemicals, and took down a bottle which he had placed on a shelf more than a year previously. It contained a red-brown evil-smelling liquid and had been obtained by him from the mother liquor of Kreuznach spring. He had put it aside for later study assuming off-hand that it was iodine chloride. Liebig never recovered from this grave disappointment, especially since never again did he have another chance to discover an element. He sought to salve his wounded vanity by sneeringly remarking, "Balard did not discover bromine, rather bromine discovered Balard", a reaction branding Liebig as a poor loser. Actually the Kreuznach apothecary Carl Löwig (1803–1890), who later was professor at Zurich and Breslau, experienced the same disappointment. He too had shown the presence of the new element in the Kreuznach mother liquor but had delayed publishing his finding pending more experiments, which he actually carried out later.

Liebig's friend, Friedrich Wöhler (1800–1882) whose fame was first founded by his isolation of aluminum in 1827, had the opportunity of discovering two hitherto unknown elements and missed both chances. In 1830 he was studying a Mexican mineral turned over to him by Alexander von Humboldt, and in which the mineralogist Del Rio of Mexico City 30 years before believed he had found an unknown element which he named "erythronium" because of the red color of its oxide and salts. However, led astray by the French chemist Collet-Descotil, Del Rio later withdrew his announcement. At this time Wöhler was recovering from an attack of hydrogen fluoride vapors and sent the specimen to his student Nils Gabriel Sefström (1787–1845) at Fahlun for further examination. The latter found that the Mexican mineral and also a certain Swedish soft iron unquestionably contained an unknown element. He named it vanadin (vanadium) in honor of the Nordic goddess Vanadis (identical with Freya the goddess of love). The letter which Berzelius sent Wöhler, both chiding and commiserating him for missing this chance, is a classic in the history of the discovery of the elements.

The other instance involved a mineral from Massachusetts, later named columbite, which was suspected of containing an unknown element. The latter was suspected of being identical with tantalum, discovered in 1802 by the Swedish chemist A. G. Ekeberg (1767–1803). Wöhler likewise was trying to clear up this question but did not carry his studies to completion. However, in 1844, Heinrich Rose (1795–1864) in Berlin showed that the disputed component in columbite was not tantalum but a new element, which he named niobium from Niobe, the daughter of Tantalus. Wöhler's reaction when he heard this news was in sharp contrast to that of Liebig when the latter learned of the discovery of discovery of bromine. Wöhler wrote to Berzelius: "I do not feel aggrieved because this has eluded me, and I heartily wish our good Heinrich every joy in the discovery."

Imagined Discoveries

Behind the scenes of the scientific research stage there can be found some peculiar types of "discoverers," who work diligently but who are imbued with the hope and firm determination some day of making a great discovery. Possessed of a fixed idea, they pursue it like a mirage, looking neither to right nor left, and eventually they come to believe that the image is the real thing. They lose the ability to make a reasoned objective judgment; they become prisoners of their own imaginations. If they then decide to appear on the stage before the public and exhibit their alleged findings, it sometimes happens that they are greeted with wondering looks and even receive recognition in some instances. However, such fame is fleeting. It quickly vanishes when faced with serious scientific scrutiny and may be transformed even into the opposite of honor provided it does not meet the milder fate of being forgotten.

No names connected with such alleged or supposed discoveries will be given here; it is sufficient to recall several cases that occurred within fairly recent times. In 1923 great excitement was aroused by the announcement that mercury had been transformed into gold by electrical action. Because of the impact of the modern theory of transmutation this claim was not rejected offhand even in authoritative circles (except by those who knew the "discoverer" intimately). Nevertheless, it took two years of intensive research to clear up the matter conclusively; several competent workers finally tracked down the source of the gold. It must be admitted that several facts that in themselves had scientific value were brought to light during these elucidating explorations.

Works of Art Not Discoveries

If in connection with the consideration of the varieties of discovery in the natural and physical sciences a look is also directed toward the problem of the purely mental discoveries, closer examination reveals that the two provinces possess basic differences. In the case of scientific discoveries—in conformity with the sense of the word—these deal with the revelation of something that was already present but which was merely not apparent to the human perception. Obvious examples are radioactivity, discovered only some six decades ago, and the more recently discovered transformation on earth of hydrogen into helium accompanied by the release of tremendous amounts of energy. Such secrets of nature remained hidden from the human mind until they were revealed to some favored investigator at some propitious time. Whether this disclosure came sooner or later had no effect on the features of what was discovered, because the latter was always there and was merely waiting to be found and recognized for what it was by the inquiring worker.

The situation is entirely different with respect to the products in the province of purely mental creativity. Such works by musicians, poets, writers, artists, and others are not already in existence, they have to be created. Whereas it is a matter of small importance who actually makes scientific discoveries, in the creative field the essential features of the work depend above all on the character and abilities of the person responsible. The masterpieces of such men as Goethe, Michelangelo, Shakespeare, Mozart, etc., happen but once and as unica are irreplaceable. They would not have been produced by anyone else. If on August 28, 1749, at Frankfurt am Main, the midwife had not expertly taken extreme measures with the apparently still-born infant until she could triumphantly call out "The boy lives," the human intermaxillary bone would have been discovered long since none the less, but there would have been no "Faust" or any of the other priceless Goethe creations. No other writer, no matter how accomplished, could have replaced them for us.

Division of CHEMICAL EDUCATION

American Chemical Society

Nominations for Office of Chairman-elect, 1959–60

EDWIN M. LARSEN, Professor, the University of Wisconsin, has served the Division as Member at Large on the Executive Committee since 1956. He has been active in all phases of the Summer Institute and Academic Year programs for high school teachers and has been a director of Institutes for several years. He has also served as a Visiting Scientist for the Division-administered NSF program. His Ph.D. from Ohio State came on top of a Wisconsin B.S. and experience in industrial inorganic chemistry. The Monsanto-administered portion of the Manhattan Project kept him busy with polonium in Dayton for most of the war years. His teaching at Madison has been in the general chemistry program, undergraduate inorganic and in his specialty at the graduate level: the transition elements. He has served *Chemical Abstracts* since 1944. Wisconsin high school teachers know him well for the role of leadership he has taken in helping them to help themselves to teach chemistry better.

JOHN F. BAXTER, Professor, University of Florida, has served the Division as secretary since 1956. He is well known to many members for his prior service as chairman of the Division's Committee on Institutes and Conferences. He has taught the chemistry course and served as director of numerous NSF-sponsored Institutes for High School Teachers in all parts of the country. His teaching and research in inorganic solution chemistry has been at Gettysburg, Washington and Lee, and Oak Ridge National Laboratory. For the past two years he has been on leave from his position as head of the General Chemistry Division at Florida to prepare the 160 films which constitute the world's first complete high school chemistry course on film. All who have seen these recognize the master teacher at work and share the pride of the ACS in a most significant contribution to science education.

(*Continued on page 232*)

Harold S. King
U. S. Army Chemical Corps Board
Army Chemical Center, Maryland

Pioneering Research on Isotopes at Harvard

It is difficult to transport one's self back forty years and to see the problems of that time through the eyes of those who were then in the vanguard of science. The very existence of isotopes, substances belonging in the same place in the periodic table but with different atomic weights, was being questioned. People were asking whether samples of an element derived from various geologic sources had different atomic weights and whether it could be possible to fractionate a single sample into portions differing in density. It seems appropriate to present early developments and concepts in the words and context of the period.

To set the stage I quote from the Presidential Address before the American Association for the Advancement of Science, delivered by T. W. Richards in December 1918:

> If ordinary lead should be found to be complicated, many, if not all, other elements should be tested. The outcome, while not in the least affecting our table of atomic weights as far as practical purposes are concerned, might lead to highly interesting theoretical conclusions.
>
> How can such remote scientific knowledge, even if it satisfies our ever-insistent intellectual curiosity, be of any practical use? Who can tell? It must be admitted that the relationship is apparently slight as regards any immediate application, but one can never know how soon any new knowledge concerning the nature of things may bear unexpected fruit. Faraday had no conception of the electric locomotive or the power plants of Niagara when he performed those crucial experiments with magnets and wires that laid the basis for the dynamo. Nearly fifty years elapsed before his experiments on electric induction in moving wires bore fruit in a practical electric lighting system; and yet more years before the trolley car, depending equally upon the principles discovered by Faraday, became an everyday occurrence.

It took only 25 years before another element, uranium, was being fractionated on a large scale to enrich it in respect to its content of U^{235}. Today the term "isotope" is at least as familiar to the school boy as "trolley car."

In this presentation, we deal with the two main series of investigations conducted at the Wolcott Gibbs Memorial Laboratory at Harvard by T. W. Richards and his co-workers. First there was a series of determinations of the atomic weights of lead from various sources to settle the question of whether isotopes really differ in respect to their atomic weights. Secondly a series of investigations was made on various properties of these several leads to determine what properties are dependent on a difference in weight or mass. These explorations developed into an intensive theoretical and laboratory study of the separation of isotopes of an "elementary substance" from each other.

Presented as part of the Symposium on Inorganic Chemists in the Nuclear Age before the Division of History of Chemistry and the Division of Inorganic Chemistry at the 134th Meeting of the American Chemical Society, Chicago, September, 1958.

The Atomic Weight of Lead of Radioactive Origin

Boltwood, Ramsay, Rutherford, Fajans, and other workers upon radioactivity pointed out that the most conclusive test concerning the then recent theory of the degeneration of radioactive elements was to be found in the determination of the atomic weights. A theory, proposed by Fajans and by Soddy, indicated that some of the places in the periodic table should perhaps include several elements different in atomic weight but very similar in other properties. Thus in the place assigned to lead we should expect to find ordinary lead and the leads produced by the disintegration of uranium, thorium, and actinium. The problem was one capable of a decisive gravimetric test; specimens of lead, consisting of different mixtures obtained from different sources, should have different atomic weights.

The determination of atomic weights involves experimental work of great refinement. Richards, building on the foundations laid by Stas, carried this branch of analytical chemistry to a point where he and his pupils, Baxter at Harvard and Hönigschmid at Munich, were recognized as the world authorities. As Richards in his Nobel Lecture on Atomic Weights stated:

> I have tried always to be sure that the substance being weighed represented all the substance which I was seeking to weigh, and nothing more; and wherever possible I have not contented myself with a hypothetical presumption that such was the case, but have endeavored to prove by special experiments, first, that nothing was lost, and, secondly, that no foreign substance had been unintentionally included.

In his devotion to accurate knowledge, Richards often quoted Plato:

> If from any art that which concerns weighing and measuring and arithmetic is taken away, how little is left of that art.

Richards said:

> Today we may paraphrase this saying as follows: "If from chemistry are taken away the atomic weights (or other numerical data representing the same definite proportions), little will remain of that science." As a science becomes more scientific it becomes more quantitative, and greater accuracy in the determination of its fundamental mathematical basis is required.

In the 40 years of labor on atomic weight determinations, Richards and his associates evaluated, revised, and substantiated the values for 60% of the then recognized elements. In the course of his revisions and refinements of earlier methods, Richards developed new methods of approach and types of apparatus. The nephelometer facilitated the exact determination of the end point of the reaction between silver and

Wolcott Gibbs Memorial Laboratory personnel in 1920. From left to right: *Front row*, Dr. Henry Krepelka, Miss Edith H. Lanman, Professor Theodore W. Richards, Miss Rosella J. Borthwick (sec.). *Middle row*, William M. Craig, Oscar C. Bridgeman, John Russel, Harold S. King, Dr. Emmett K. Carver. *Back row*, Charles P. Smyth, A. Sprague Coolidge, William Manning (jan.), Sylvester Boyer.

halogen ions. His famous bottling device permitted the handling of analytical material without danger either of contamination or loss. The complete technique for the precipitation of silver halide stands as perhaps the most precise gravimetric method known to analytical chemistry.

This internationally acclaimed pre-eminence in the field of atomic weights made it only natural for those interested in isotopes to turn to Richards for the determination of the atomic weights of lead of radioactive origin. Early in 1913, when the hypothesis of radioactive disintegration had assumed definite shape, Fajans' assistant, Max Lembert, journeyed to Cambridge, bringing a large quantity of lead from radioactive sources, in order that its atomic weight might be determined by Harvard methods with the precision attainable there. Ramsay also had urged on the behalf of Soddy that the atomic weight of radioactive lead should be studied at the Wolcott Gibbs Memorial Laboratory. Material to work with came from many sources, sent by those anxious to aid in this crucial test. Fajans sent a sample from Colorado carnotite and another from Bohemian pitchblende; Ramsay, a sample from the residues from pitchblende mined at Cornwall; Boltwood, a sample of lead from Ceylonese thorianite; Miner, a similar sample also from thorianite of Ceylon. The sample of purest radioactive origin was one obtained by Gleditsch from selected uraninite of North Carolina. The Carnegie Institution of Washington gave generous pecuniary assistance.

These samples were converted into lead chloride of utmost purity. In each case the lead chloride was weighed and dissolved in water. To this was added a weighed quantity of silver (as nitrate). The amount of silver exactly equivalent to the chloride was found, then an excess of dissolved silver was added in order to precipitate the dissolved silver chloride and the precipitate was filtered off, fused, and weighed. These procedures, with all the refinements stemming from long experience, gave the ratios, $PbCl_2$:2Ag and $PbCl_2$:2AgCl. In exactly the same way samples of common nonradioactive lead were analyzed, for this was not an experiment to determine the true atomic weight of lead but to show whether radioactive lead differs in atomic weight from ordinary lead.

The samples from radioactive sources possessed a slight radioactivity so one sample of ordinary lead was contaminated purposely with radium D. Since the atomic weight of this contaminated sample was exactly like the average for ordinary lead, it was evident that the analytical process was not affected by the mere presence of radioactivity.

Lead from the various sources gave atomic weights ranging from 206.8 to 206.4, the last being derived from the North Carolina uraninite. Common lead gave a value of 207.15. These values show conclusively that lead from various radioactive sources differs in atomic weight from ordinary lead and that different samples give different values, probably due to admixture with ordinary lead. This was confirmed by a later analysis in which Richards and Wadsworth determined the atomic weight of a sample of lead obtained by Professor Gleditsch of the University of Kristiania from very old and very unaltered cleveite found in well-developed cubic crystals in the pegmatite dykes of Norway. This sample gave an atomic weight of 206.08, very near the theoretical for the pure end product of the radioactive disintegration of uranium.

Comparison of Properties of Different Kinds of Lead

On the basis of the quantitative results of the atomic weight determinations, Richards was convinced that here was one real difference between lead from uraniferous ores and common lead. The possession at the Wolcott Gibbs Memorial Laboratory of stocks of uranium lead, especially a large quantity from the Olary mines of South Australia with an atomic weight of 206.34, made possible comparison of other properties of uranium lead and ordinary lead. These investigations were done with the aid of several student assistants, including C. Wadsworth 3d, W. C. Schumb, and N. F. Hall.

It was found that the density of lead and the solubility of lead nitrate were very nearly proportional to the atomic weights. For the metals, the atomic volume, melting point and electromotive force at a heated junction were very closely, if not exactly alike. The spectrum lines produced by the two sorts of lead were so precisely alike, both as to their wavelengths and their intensities, that ordinary spectrum analysis showed no difference whatever. The molecular solubility and refractive index of the nitrates also were essentially identical for the two isotopes of lead.

Attempts to Fractionate Mixed Isotopes of Lead

From the data at hand Richards concluded that at least two kinds of lead exist, one the ordinary metal disseminated throughout the world in nonuraniferous ores; another a form of lead apparently produced by the decomposition of uranium. The two kinds had been shown to be closely if not exactly alike in every respect except atomic weight, density, and immediately related properties involving weight. Left unanswered was the nature of ordinary lead. It might be a pure substance with an atomic weight of approximately 207.2 or it might be a mixture of uranium

lead with lead of higher atomic weight, perhaps 208, formed by the disintegration of thorium, for which Soddy and Hönigschmid had found quantitative evidence in thorium minerals. Clarke had pointed out that ordinary lead may be the product of a far earlier synthesis or evolution from smaller atoms. Richards stated his views as follows:

> Whenever, in the inconceivably distant past, the element lead was evolved, it is hardly to be supposed that uranium-lead and thorium-lead could have been entirely absent. The conditions must have been chaotic and favorable to mixture. When the two or more forms were mixed, none of the processes of nature would separate them. Therefore they must appear eons afterwards in an equably mixed state on earth constituting our ordinary lead.

Characteristically, Richards continued:

> The true answers to these questions are not to be found in speculation. They are to be found by careful observation. For example, the doubt as to the nature of ordinary lead can only be decided by discovering whether or not it may be separated into two constituents. Since weight (or mass) is the quality distinguishing between the several isotopes or kinds of lead, weight (or mass) must be made the basis of separation.

The process for fractional crystallization was one that had reached a high stage of perfection at Harvard, having been used repeatedly by Baxter in purifying the rare earths preparatory to the determination of their atomic weights. Since this process had not previously been used for the fractionation of isotopes to the degree that had been found necessary in the case of the rare earths, Richards with the help of N. F. Hall conducted over one thousand fractional crystallizations of a sample of lead nitrate, derived from Australian carnotite, containing one part of ordinary lead to three parts of radium G with a mere trace of radium D. The atomic weights of samples obtained from the crystal and mother liquor ends of the series agreed within an experimental error of six parts in one hundred thousand and the beta-ray activities within the experimental error of 1%. The outcome gave strong experimental support for the hypothesis that isotopes are really inseparable by any such process as crystallization.

While still an undergraduate at Harvard, I was intensely interested in the work on isotopes then being pursued by Professor Richards. In studying the Grignard reaction I came upon a reference to organo-lead compounds and especially to the highly volatile tetramethyl lead which seemed an ideal substance for fractional diffusion. On further reading references were found to conflicting claims that in the action of a Grignard agent on lead chloride a partial separation of isotopes took place. I submitted these ideas to Professor Richards in 1918, and he offered me an opportunity of working under him at Gibbs Laboratory at the conclusion of World War I.

At first an exhaustive study was made of the theory of fractional diffusion. It was found that because of the high molecular weight of tetramethyl lead and the slight difference in the masses of the two most important isotopes, attempts based on fractional diffusion of tetramethyl lead were out of the question with the means at our disposal. Furthermore, the toxicity of tetramethyl lead imposed an unwarranted hazard.

Thus we turned our attention to the action of a Grignard reagent on lead chloride. Because of conflicting results of previous investigators a definitive test seemed required. Moreover, theoretical considerations made this reaction worthy of investigation. It appeared that the reaction,

$$2PbCl_2 + 4RMgBr = Pb + R_4Pb + 2MgCl_2 + 2MgBr_2$$

occurs in two stages with the intermediate formation of R_2Pb which associates to some extent to R_2PbPbR_2. This presumably decomposes to $R_4Pb + Pb$. If the two lead atoms in this compound were identical, then one would be as likely to take the metallic form as the other. If the two lead atoms were isotopic, one having a greater mass than the other, mass might produce a slight difference, causing a preferential elimination of one of the lead atoms. Accordingly a series of fractionations was made starting with ordinary lead chloride. The end fractions were analyzed by L. P. Hall. The atomic weight of the extreme lead fraction was 207.217, and of the extreme tetraphenyl lead fraction, 207.219. No separation was apparent.

At the suggestion of Langmuir, still another method was investigated, that of irreversible evaporation of metallic lead at a comparatively low temperature in an X-ray vacuum. Over 1300 grams of ordinary lead were heated in 22 gram lots until a well-defined spot of condensate appeared. In this way a total of 31 grams of evaporated lead was obtained. In another series of irreversible evaporations, 80 grams of lead from Australian carnotite were fractionated into two equal fractions and each of these further fractionated. Again L. P. Hall did the analyses. He found that no appreciable separation had occurred in either series of fractionations.

Thus comes to an end the researches on the separation of isotopes conducted under the direction of T. W. Richards. That the results were negative is now not surprising, but they were necessary in clearing the ground for further work.

* * *

I have heard people say how tragic it was for Richards to have his life work superseded by the physical methods such as those devised by Aston and others. From my association with Richards, I do not think he looked at it in this light. He welcomed new ideas but insisted that they be subject to searching proof. He knew that facts were immortal, and that others would undoubtedly add to the structure he had erected on the foundation laid by Stas.

I will conclude with the final statement of Richards in his Nobel award lecture:

> As you have just seen, the more recent researches have improved upon those of Stas. In years to come, let us hope that yet finer means of research and yet deeper chemical knowledge may make possible further improvements, yielding for mankind a more profound and far-reaching knowledge of the secrets of the wonderful universe in which our lot is cast.

* * *

Harold G. Cassidy
Yale University
New Haven, Connecticut

Chemical Compounds Isolated from Tubercle and Other Acid-Fast Bacilli

In the great front hall on the second floor of the Sterling Chemistry Laboratory of Yale University there hangs an unusual exhibit (Fig. 1). There is no other exhibit of this nature in the world. It is at once a monument to a vision and to the tenacious purpose which implemented this vision, and a record of the program which developed from and through this vision.

In a glass-fronted case some 28 feet long are arranged 41 cards. Each card records a chemical investigation of a substance obtained from specially grown and solvent-extracted acid-fast bacteria of a particular kind. The substance investigated is placed in a horizontal, sealed tube, at the top of the card (Fig. 2). The fractions into which it was separated are arranged in sealed tubes, vertically placed, below it. Everything is labeled and authentic. Many of the cards represent efforts of students which led to dissertations, for during the program of investigation represented by this exhibit 33 graduate students and postdoctoral fellows advanced their education.

The history of this exhibit is fascinating. It begins with Dr. William Charles White, at the time chairman of the Medical Research Committee of the National Tuberculosis Association. His committee had supported work done by Professor Treat B. Johnson and his students on proteins and nucleic acids of tubercle bacteria. This work was aimed at learning about the chemistry of these bacteria so as (hopefully) to develop a cure for tuberculosis. The time was the early 1920's. In 1924, Alfred F. Hess and Harry Steenbock independently discovered that certain sterols when irradiated with ultraviolet light became useful in treating rickets. This discovery focused attention upon the steroids—substances about which very little was known at the time.

Dr. White saw that here was an important group of substances that should be examined in connection with the exploration of the chemistry of tubercle bacteria, and looked for someone with the requisite temerity who was willing to undertake the work. An interesting chain of events brought such a man to his attention.

Dr. Rudolph J. Anderson, who had been working at the New York Agricultural Experiment Station since 1911, had been given leave to visit Europe, serve in the U. S. Army for a year and a half during the war, and earn a Ph.D. degree from Cornell. When he returned to the station he cast about for an interesting problem. At that time only two plant nucleic acids were known. These had been isolated from yeast by P. A. Levine and from wheat-germ by T. B. Osborn, and they seemed most interesting substances. What would correspond as a source which would interest an agricultural experiment station? A corn crop is important, and, Dr. Anderson says, the corn pollen seemed to him a likely source of nucleic acid, since it corresponded to sperm—which had been shown to be a good source. Obtaining permission to cut the ripe tassel off of every other cornstalk in the Geneva field, Dr. Anderson harvested his product. The tassels were laid on paper to dry, then the pollen was shaken out and sifted to remove bits of leaves, and other matter. He thus obtained *one kilogram* of the pollen, which he says had a fragrant and interesting odor. Tests with some of the pollen, using extraction with mildly alkaline water yielded nothing. This implied a coating which prevented extraction of the nucleic acid, so alcohol was tried. To his great surprise, a large amount of wax-like material was obtained, amounting to about 25% of the weight of the original dry pollen. Now it certainly seemed that any material that made up a quarter of the weight of the pollen must be important, so the residue was set aside.

This new material contained oxygen, and thus the possibility of an ester was suggested. Saponification of a sample yielded a new sterol, together with palmitic acid. Thus began for Dr. Anderson an interest in the lipides, or fat-soluble constituents, of plant materials. He examined various parts of grains, but found nothing like this new sterol. While visiting in California a colleague gave him some hundred grams of a supposedly pure sterol "sitosterol." To examine it he acetylated the hydroxyl group and recrystallized the product. Its properties changed on recrystallization so that after 60

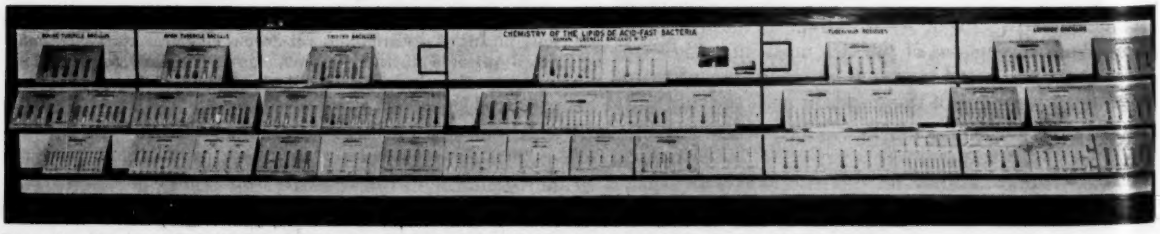


Figure 1. Case containing fractions obtained in the study of the lipids of acid-fast bacteria. Photo by Philip Blume.

recrystallizations a dextrorotatory fraction was obtained from what had been a levorotatory mixture.

Some of this work was reported at a meeting in New Haven, and T. B. Osborn got interested enough to send Dr. Anderson a sample of sterol which he had obtained in the preparation of zein. On working this up, a crystalline product with no rotation was obtained—apparently a new sterol. But the intuition of a natural-products chemist suggested further recrystallizations and after ten more, the sample was separated into dextro and levorotatory fractions. The intuition, says Dr. Anderson, had not prevented his sending to a journal a preliminary communication about his work, and this had to be held up temporarily in galley form while the dextro and levo fractions were examined.

This work evidently made him an expert on steroids, for at the first Organic Symposium, when he was asked to submit titles for two papers, one of which was to be chosen for presentation, he was finally asked to talk on the new subject of sterols, although the other subject whose title he submitted—which was the anthocyanins of grapes—was the one he had preferred. He had been proud of this work in which he had established that syringic acid was present. But he spoke on sterols, and was heard by Professor T. B. Johnson of Yale who at the time was, as we said, connected with Dr. William C. White.

Dr. White, pursuing his vision of a thorough study of the chemistry of the tubercle bacillus, negotiated for Dr. Anderson to study its sterols, and with Yale University to enter upon fruitful cooperation in this venture. But there turned out to be no sterols in tubercle bacteria!

The bacteria were grown on the Long synthetic medium at the H. K. Mulford and Company plant in Philadelphia. The first batch was grown in 200 one-liter culture-bottles. When the live bacteria were ready for harvesting Dr. Anderson went to the plant and he and Mr. John Glenn filtered them off. The yield was disappointingly small, yet this was a rather large operation for that period. It was obvious that more material had to be obtained, and upon authorization, a batch ten times larger was started. In two months it was ready for harvesting, and after a day of hard work, filtering the quantities of cultures through Büchner funnels (without filter papers because the colonies of bacteria held together in masses) Dr. Anderson returned to New Haven with five five-gallon bottles of bacteria suspended in alcohol.

It is perhaps hard for the younger chemist nowadays, with his paper and gas chromatography, microtechnique, and infrared, to imagine the work involved in 1926 in a problem of this nature. The sheer physical labor of handling five-gallon batches of solvents in the laboratory, of filtering, distilling, and recovering precious solvents. It was six months before the five five-gallon bottles yielded material to be analyzed. And then there were no sterols.

But there were quantities of waxy materials, composed of new and unusual constituents, among which was the intriguing previously unknown, high molecular weight mycolic acid.

For Dr. White these were exciting discoveries since they implied unusual properties to the human tubercle bacterium. This bacterium is "acid-fast" in that it takes up a dyestuff so firmly that it cannot be leached out by acid. He provided further support for the work so as to examine other pathogenic acid-fast bacteria: bovine and avian tubercle bacilli, leprosy bacillus and, for comparison, a non-pathogenic acid-fast bacterium, the timothy-grass bacterium. The idea was to see if possible wherein these all differed. Why was one non-pathogenic, one pathogenic to humans, another to cattle, another to birds? The search for an answer to this question motivated the work. It progressed from 1926 on, and material was collected. In 1943 the exhibit shown in Figure 1 was completed, and it was presented to Yale University on February 3, 1944. It seems appropriate to call attention to this unusual exhibit, and to preserve, as a human and scientific document, Dr. Anderson's remarks when the exhibit was placed in the custody of Yale University.

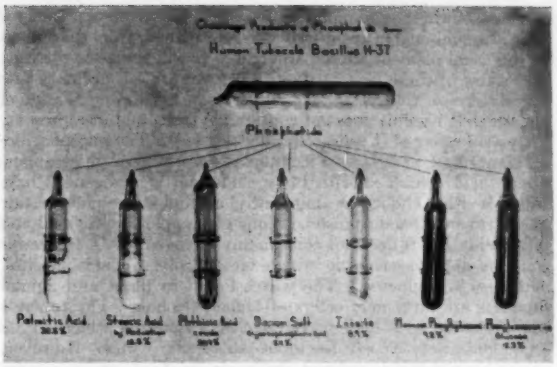


Figure 2. One of the cards on which samples of fractions are mounted permanently in sealed tubes. Photo by James Spambanato.

I want to mention briefly something about the work involved in preparing this collection. It represents seventeen years of continuous research on the chemistry of the lipids or ether-soluble compounds of the tubercle bacillus. The work has been a cooperative undertaking between Yale University and the Committee on Medical Research of the National Tuberculosis Association.

All of the specimens shown in the collection are authentic chemical compounds isolated from the tubercle bacillus and some other acid-fast bacteria. A study of the collection will indicate the plan that has been followed in the investigations. Samples of the various substances that have been isolated have been placed in sealed glass tubes and mounted on cards. Each card represents a complete investigation. The substance investigated is indicated by the tube at the top of the card while the products obtained are shown in tubes arranged underneath. The exhibit is therefore self explanatory. The living organisms were used as starting material in every case. The bacteria were extracted with suitable solvents and eventually the substances contained in the extracts were separated into a number of primary fractions, namely fats, phosphatides, and waxes. Each of these primary fractions was purified, analyzed, and hydrolyzed. The eventual cleavage products of these primary fractions were then separated and purified as thoroughly as possible until apparently pure compounds were obtained. Many of these compounds were further studied in order to determine their chemical structure.

Several of the cleavage products represent a series of new and previously unknown chemical compounds such as tuberculostearic acid, phthioic acid, mycolic acid, several levorotatory acids, the pigment phthiocol, the alcohol phthiocerol, and several specific polysaccharides. The work of Dr. Sabin has shown that certain of these compounds, notably phthioic acid, possess specific biological properties, and this is probably due to the unusual chemical structure that these substances possess.

Many of the cleavage products, both fatty acids and carbohydrates, are identical with substances found both in plants and

animals, but in the compounds isolated from the tubercle bacillus they are combined in an entirely different manner from that found in the usual plant or animal kingdom. It will suffice to mention just a few of these peculiarities. For instance, all ordinary fats are glycerides, that is, fatty acid esters of glycerol. The fat of the tubercle bacillus does not contain any glycerol but represents fatty acid esters of the disaccharide trehalose. The phosphatides of plants and animals are compounds containing glycerophosphoric acid combined with fatty acids and a nitrogenous base which is either choline or amino ethyl alcohol. The phosphatide of the tubercle bacillus also contains glycerophosphoric acid and fatty acids, but it does not contain any nitrogen base. Instead it contains a polysaccharide which on hydrolysis yields inositol, mannose, and glucose. The waxes found in plant and animal products are fatty acid esters of higher alcohols. The tubercle bacillus contains a high percentage of a material which in its crude state very closely resembles an ordinary wax. However, when this material is purified and analyzed it is found to consist of a combination of a specific polysaccharide with mycolic acid, together with certain levorotatory acids and the specific alcohol phthiocerol. It is evident, therefore, that substances contained in the tubercle bacillus such as fats, phosphatides, and waxes differ entirely in composition and structure from previously known analogous compounds.

The chemical investigations have shown that the human tubercle bacillus differs from the other acid-fast bacteria, since it is the only organism that contains phthioic acid. There is, however, a resemblance between the human and the bovine types of tubercle bacilli, because the wax of both organisms contain mycolic acid and the alcohol phthiocerol.

The other acid-fast bacteria that we have analyzed contain different compounds from those occurring in the human tubercle bacillus. There is a resemblance, however, between the avian and timothy grass bacillus and the leprosy bacillus because the waxes of these organisms contain two identical new higher alcohols.

It has been a long, slow process to establish the facts I have just mentioned. When the investigation was first begun neither I nor anyone else had any definite knowledge about these substances. Even now we probably know only a part of the story, but at least a beginning has been made. I believe that all future investigations on the lipides of the tubercle bacillus will have to start where we leave off. It is appropriate, therefore, to dedicate this collection as a permanent source of reference for future investigators, and Yale University will act as custodian.

Doctor White, the chief credit for this collection belongs to you. The first time that I met you with Doctor Johnson in this laboratory in March, 1926, you stated clearly that you considered it of great importance for the proper understanding of the pathology of tuberculosis to establish a base line of the chemical units contained in the tubercle bacillus. For comparison with the human tubercle bacillus you indicated that the bovine and avian types of tubercle bacilli should also be analyzed by the same methods. Later on the leprosy bacillus and the non-pathogenic timothy grass bacillus were through your efforts included in the investigation. The base line was thus extended to contain five different strains of acid-fast bacteria.

In carrying out this work I have attempted to follow your original idea in order that you might realize in some measure your ambition to establish a base line of the chemical units contained in the tubercle bacillus.

In conclusion I want to pay a warm tribute to all the persons who have collaborated with me in this work. This is not a one man show. Since this work began I have enjoyed the faithful collaboration of 33 assistants: 21 of them came from the U.S.A., 2 came from Germany, 2 from Hungary, 1 from Austria, 1 from Russia, 1 from Poland, 1 from Japan, 1 from China, 1 from Formosa, and 1 came from Sweden. I mention these co-workers by name:

M. L. Burt, Henrick Bjorling, James Cason, H. G. Cassidy, L. H. Chang, E. Chargaff, M. M. Creighton, J. A. Crowder, G. I. deSuto-Nagy, C. O. Edens, N. Fethke, W. B. Geiger Jr., L. G. Ginger, Shang-lieh Liu, Alex Lesuk, W. C. Lothrop, S. Ludewig, A. J. McAmis, H. duMont, M. S. Newman, M. C. Pangborn, R. L. Peck, R. E. Reeves, A. G. Renfrew, E. Gilman Roberts, D. H. Saunders, George Scheff, M. A. Spielman, F. H. Stodola, D. M. Tennent, N. Uyei, S. F. Velick, C. W. Wieghard.

They have all contributed their devoted labors to the success of this rather unusual and unique cooperative research but I must mention especially Dr. L. G. Ginger who last year spent much time and care in arranging and cataloguing this exhibit. I thank them one and all for their help and assistance.

The presentation of the exhibit was made by Dr. Lewis J. Moorman, President of the National Tuberculosis Association, and it was accepted for Yale by Mr. Carl Lohman, Secretary to the University. Dr. William Charles White, whose suggestions started the investigation, was present. Since its receipt, this unusual exhibit has been visited by many students and researchers. It is one of the evidences we have of the link between teaching and research.

Recently, in a conversation with Dr. Orville F. Rogers, former Director of the Yale University Department of Health, Dr. Manfred L. Karnovsky, of the Harvard Medical School spoke of how he and his co-workers had profited from the work of Dr. Anderson. "I told him," he recalls, "how fundamental Dr. Anderson's classic work has been to all our thinking. In addition to the study mentioned on the interrelationship between the metabolic activities of the tubercle bacillus and the host cell, we have slowly been examining the patterns of labeling in several fractions of the tubercle bacillus grown on various radioactive substrates. In this project Dr. Anderson's work is the cornerstone of our endeavor."

It is good to have available to us such cornerstones. They give some hint of the labor, devotion, and vision that go into shaping the cathedrals of science. They are a present source of encouragement and inspiration.

A Molality-Molarity Paradox?

Consider w grams of a solute of molecular weight p dissolved in W grams of a solvent to form a solution of density d grams per ml. Then the molality $m = 1000w/pW$ and the molarity $M = 1000wd/p(W + w)$.

Suppose we have a solution such that the molality equals the molarity. It then follows that $w = W(d - 1)$. It is possible, at least in principle, for m to be equal to M in a nonaqueous solution where d is greater than unity, providing components with suitable partial molar volumes are chosen. The case where d approaches unity corresponds to a very dilute aqueous solution when m approaches M. An impossible situation develops, however, when d is less than unity; yet there seems no obvious reason why m could not equal M in a solution for which d is less than unity.

(*See page 248*)

The Lavoisier Collection at the Conservatoire National des Arts et Métiers

M. Daumas
Rue St. Martin, Paris, France
Translated by **Gregory D. Seaman**
College of Wooster, Wooster, Ohio

The chemistry section of the Musée du Conservatoire National des Arts et Métiers once provided an up-to-date view of the chemical industry. It was established during the nineteenth century using models or patterns of apparatus principally from the mineral chemical industry and the gas lighting industry. The traditional industries, such as those producing starch, sugar, stearin, and brewery products, were also very well represented.

Since 1900, gifts to this section of the museum have stopped, so that fewer original models have been used. The rapid evolution of the chemical industry which appeared at the end of World War I has not been followed by a transformation of the chemistry section. Consequently this has taken on more and more a historical character.

The addition of Lavoisier's apparatus about 40 years ago greatly increased the historical interest of the chemistry section. All of the laboratory equipment and all of his papers were turned over after the death of Mme. Lavoisier to one of her nieces, Mme. de Chazelles. They were kept for a long time in a chateau near Clermont-Ferrand. Leon de Chazelles gave some important items to the Academie de Sciences, along with all of the scientific papers and laboratory records. In 1866, the Academie likewise gave the Lavoisier apparatus that it had housed to the Conservatoire National des Arts et Métiers, along with numerous other instruments that had been received since the beginning of the nineteenth century and for which it no longer had room.

This first gift was responsible for the dedication of a particular room in the museum to Lavoisier; it is called the Echo, at the base of the stairs of honor. It displays, among other things, the gasometers constructed by Mégnié in 1787, two great lead tanks for handling gases, the original flask used for the synthesis of water, the two calorimeters, the apparatus for studying the composition of oils, alcoholic fermentation (see Fig. 1), and putrid fermentation, which are described in the *Traité élémentaire de Chimie*, as well as some ordinary balances, some barometers, and a collection of hydrometers.

In 1952 Mme. Vanssay de Chazelles, who had inherited the Lavoisier apparatus, sold the collection to M. du Pont de Nemours, who gave it to the French government. The latter has entrusted it to the care of the Conservatoire National des Arts et Métiers.

EDITOR'S NOTE: This is another in the series of papers being solicited by Dr. RALPH E. OESPER to give those of our readers who may be crossing the Atlantic a preview of places of notable scientific interest. Mr. Seaman, the translator, is a senior majoring in physics at the College of Wooster. See also: J. CHEM. EDUC. **34**, 283, 607 (1957) and **35**, 300 (1958).

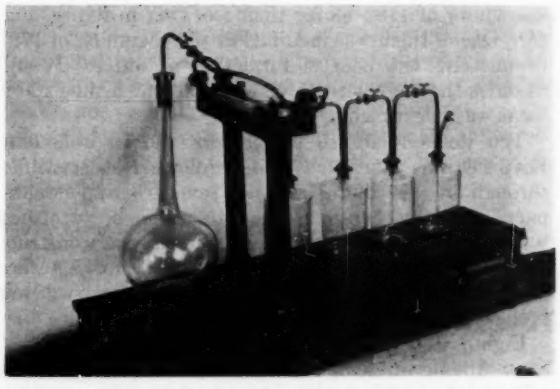


Figure 1. Apparatus for vinous fermentation, constructed by Fortin in 1788, and described in the *Traité*.

The inventory of the collection contains nearly 400 items, which are distributed as follows:

About 20 items relate to balances, weighing instruments, weights, etc. Special attention should be drawn to the two precision balances by Mégnié and the great precision balance by Fortin, which are described in *Traité élémentaire de Chimie* (see Fig. 2). There are also some ancient weights, based on an eight-ounce pound, that were divided into decimal fractions by Fourché, balance-maker to the mint, commissioned by Lavoisier. Several balances are of the current type with two equal beams, and one of these must be the balance of Chemin that Lavoisier used in 1770 for his experiment proving that water cannot be changed into earth by prolonged boiling.

About 30 items relate to thermometers and calorim-

Figure 2. Large precision balance constructed by Fortin in 1788. This balance was placed at the disposal of the Commission of Weights and Measures which established the metric system.

etry apparatus. The thermometers have been described at length by Trucot in "Les Instruments de Lavoisier," *Annals de Chimie et de Physique* [5] **18**, 289. Several are signed by Cappy and Mossy. The latter made two identical thermometers, one of which was deposited by Lavoisier in 1783 in the cellar of the Observatory of Paris, while the other is in the collection at the Conservatoire. Several thermometers are made from preliminary sketches, with special vernier scales.

The two most remarkable items in this category are the two calorimeters used by Lavoisier and Laplace in the winter of 1782–83 for their work on heat (see Fig. 3). One of them was modified at the beginning of 1787 to measure the heat of formation of water. It still includes the flask with three tubes in which the experiment was performed.

Ten items relate to barometers and hydrometers. Lavoisier was interested in meterological observations throughout his life. He had some correspondents, particularly in eastern France, to whom he furnished some instruments. In 1779 he had Mégnié construct eight barometers of a special type, several of which were distributed to his correspondents. Number two and four of this special series are in the Conservatoire.

Eighty items relate to glassware, containers, tubes, etc. Among these is the apparatus depicted on the table in the great David portrait of Lavoisier and his wife. (The portrait is now at the Rockefeller Institute in New York.) The purpose of the apparatus has not yet been determined.

The collection also includes two air-pumps, some mirrors and lenses, some hydrostatic and electrical demonstration apparatus, a Ramsden type electrostatic machine, a Dellebarre type microscope, some laboratory oil burners, and a great number of small personal objects used by Lavoisier in the laboratory: fire-lighting equipment, corrective lenses and spectacles, protective face masks for calcinations, spatulas, knives, wooden stands, etc.

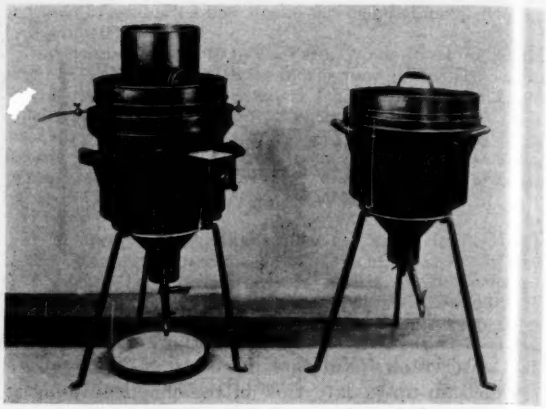


Figure 3. Calorimeter used by Lavoisier and Laplace for their research on heat from 1782–87. On the left the calorimeter is modified for measuring the heat of formation of water.

Many of the objects acquired in 1952 were not in good condition. It has been possible to restore certain things, which are now on display in the Echo room.

A purchase and a more recent gift have brought to the museum two mahogany tables that Lavoisier had made by the cabinetmaker Jacob for his three precision balances, his large laboratory table, and his great work desk with a cylinder bearing the signature of the cabinetmaker Caumont.

The Conservatoire des Arts et Métiers now possesses the whole of Lavoisier's laboratory instruments and furniture still in existence. A descriptive catalogue of his collection is being prepared.

Some of the great French chemists have been professors at the Conservatoire, and their apparatus has been used by J. J. Schloesing (1824–1919) and his son, A. Théophile Schloesing (1856–1930), in their study of the composition of arable soils and the reactions which produce them. There is also some of J. B. Boussingault's apparatus for work on chemical agronomy.

Division of CHEMICAL EDUCATION

American Chemical Society

Nominations for Secretary, 1959–60

JACK G. CALVERT, Associate Professor, Ohio State University, has served the Division for three years on the Program Committee (chairman in 1958). The excellence of recent symposia reflects the fortunate combination of his active interest in research with a parallel conviction that good teaching depends on a knowledge of new developments. A Californian with degrees from UCLA, Dr. Calvert has had postdoctoral fellowships at Ottawa and has been a consultant with government laboratories. His research interest is photochemistry and reaction kinetics. At Columbus his teaching responsibilities have been general chemistry, physical chemistry, and graduate-level courses in his specialty. ACS student affiliates and Phi Lambda Upsilon at Ohio State have thrived during his terms as faculty sponsor.

WILLIAM B. COOK, Professor and Department Chairman at Montana State, currently heads the Division's important and busy Committee on Institutes and Conferences. He has also served for several years on the Committee on Teaching of Chemistry. As a further contribution to the many functions of the Division, he has been one of its Visiting Scientists. Texas-born and trained, he earned further degrees at Colorado and Wyoming. He stayed on to teach at Laramie until Baylor called him home in 1953. The NSF lured him to Washington for a brief stay before he again went west to his present position in 1957. Organic chemistry, especially alkaloids and nucleophilic aromatic displacement reactions, is his research interest. His dynamic teaching is known for the use of ingenious devices to help students visualize chemical theory.

(*Continued on page 241*)

George E. Kimball
Arthur D. Little, Inc.
Cambridge 40, Massachusetts
and **Ernest M. Loebl**
Polytechnic Institute of Brooklyn
Brooklyn 1, New York

A Quantum Mechanical Theory of Complex Ion Formation

The electrostatic nature of binding

This paper will concern itself with the present state of the theory of chemical binding of coordination compounds in general and of the complexes formed by the transition metals in particular.

Before quantum mechanics was developed, most of the discussion of coordination compounds was in terms of rather simple electrostatic models, developed particularly by Sidgwick and Fajans. The complex was considered as composed of a central positive ion, which attracted the ligands to itself by electrostatic forces. If the ligands were themselves negative ions, the attraction was simply the attraction of the opposite charges. If the ligands were such neutral molecules as H_2O or NH_3, the attraction was ascribed to the dipole moments of such molecules. The various ions and molecules were usually thought of as spheres of definite radius. The water molecule, for example, was a sphere with a dipole at its center. Polarization effects were thought of as producing dipole moments, and these dipole moments were treated as if there were ideal dipoles at the centers of the polarized molecules.

These very simple concepts suffice to explain a great many experimental facts amazingly well. In many cases, however, the predictions of these theories are at variance with the facts not only quantitatively but even qualitatively. It is sometimes supposed, quite erroneously, that the fault lies in the fundamental, classical picture with its assumption of electrostatic forces only and that quantum mechanics remedies this by the introduction of new forces, which have no classical counterpart, such as "valence forces," "exchange forces," or "resonance." This is not the case. It cannot be too strongly emphasized that the only forces of sufficient importance to be considered are still electrostatic forces only.

The real reason for the failure of the simple model in many cases lies in the neglect of the nonspherical form of many molecules and of the easy deformability of many of those that are spherical. Furthermore, the forces between aggregates of electric charge can be successfully approximated by those between ideal dipoles only when the distance between the aggregates is large. In the close packed arrangement of a complex ion the approximation does not even converge. Because of these two difficulties the simple model could not be expected to do well.

Much of the progress which has been credited to quantum mechanics has in fact been due to the overcoming of these difficulties. The description of the electron cloud of the central ion in terms of *s*, *p*, *d* orbitals can be looked upon as a device for getting away from spherical symmetry. The formation of molecular orbitals is a way of expressing the problem of packing the ligands around the central ion, and such few energy calculations as have been made have treated the interactions of the electron clouds without the resort to idealized dipoles.

Presented in part at the Symposium on Advances in Chelate Chemistry, New York, April 29–30, 1955.

Wave Functions and What They Mean

The application of quantum mechanics to the elucidation of the structure of coordination compounds starts with the same general principle as its application to any other problem.

We can take as our starting point the Schrödinger equation for stationary state, $H\Psi = E\Psi$ (*1*), where H is the Hamiltonian operator,[1] E the total energy of the system, and Ψ ("the wave function") a function of all the coordinates of all the electrons whose square indicates the probability of finding the electrons in various space elements. Another, and very useful, interpretation of Ψ is this: If we give up the idea of the electrons being point charges and imagine their charges to be "smeared out" over space, then Ψ^2 is a measure of the local density of this charge distribution.

Mathematically, the Schrödinger equation is a differential equation whose solutions are the wave functions Ψ. Owing to the physical meaning of Ψ most solutions are unacceptable. Acceptable (i.e., physically meaningful) solutions exist only for certain values of the parameter E, i.e., certain values of the total energy of the system (*2*).

In principle, the solution of a problem then proceeds as follows: The Schrödinger equation is set up (this is, even for complicated problems, a relatively simple and straightforward matter) and the set of acceptable solutions found. The values of E so found

[1] To see that quantum mechanics does not involve the introduction of new, nonclassical energies, we consider that the Hamiltonian operator is derived from the classical Hamiltonian function for the same problem by the substitution of certain linear operators for the coordinate and momentum variables. The only potential energy term of any importance which the classical Hamiltonian contains in the cases under discussion is coulombic (electrostatic) energy and therefore only electrostatic potential energy appears in the quantum-mechanical Hamiltonian. Since, according to the virial theorem (Eyring, Walter, Kimball, p. 355; Schiff, p. 140), valid in quantum mechanics as well as in classical theory, the average kinetic energy at equilibrium is $-\frac{1}{2}\bar{V}$ where $\bar{V}$ is the average potential energy, it follows that the total energy of the system is completely determined by this electrostatic potential energy. This statement neglects the quantum-mechanical phenomenon of spin which has no classical counterpart; however, it can be shown that the direct influence of spin on the energy is so small as to be negligible in a qualitative or semiquantitative discussion.

give the different energies the system may have, and the corresponding Ψ's, indicating the corresponding electron distributions, give a complete description of the system including all the information that is experimentally obtainable.

The difficulty is that although we are convinced of the existence of solutions to the Schrödinger equation, it is prohibitively difficult to find them. Very drastic simplifications have therefore to be resorted to to find approximations to these solutions. A major difficulty is due to the fact that Ψ is a function of many variables whose number depends on the number of electrons. The magnitude of this difficulty can be gathered from the fact that no complete solution for a system containing more than one electron has yet been found. The way one tries to circumvent this difficulty is by expressing Ψ as a product of functions, each one of which is a function of the coordinates of one electron only, i.e., setting

$$\Psi(1,2.....n) = \psi_1(1)\ \ \psi_2(2)\ \ \psi_3(3).....\psi_n(n)$$

where 1,2, etc. stand for the coordinates (including the spin coordinate) of the first, second, etc. electrons, respectively. Such a simple product wave function can, however, never be an acceptable approximation for a very fundamental reason: Its use violates the indistinguishability of the electrons and the Pauli exclusion principle (*3*). To avoid this, we have to choose as our approximation a particular sum of such product wave functions as the above.

For instance, if ψ_1 and ψ_2 are different functions, then $\Psi(1,2) = \psi_1(1)\psi_2(2)$ or $\psi_1(2)\psi_2(1)$ are not acceptable functions since their squares change their values when the labels of electrons one and two are interchanged and hence the electrons appear distinguishable. However, the linear combinations (sums) $\psi_1(1)\psi_2(2) + \psi_1(2)\psi_2(1)$ and $\psi_1(1)\psi_2(2) - \psi_1(2)\psi_2(1)$ conserve the indistinguishability since the values of their squares are unchanged when the labels are interchanged. The Pauli principle can be expressed as an assertion that only those wave functions which change sign (are antisymmetric) when any two electrons are interchanged describe existing states. Hence, in the example above only the second sum is acceptable. It can be shown that such an antisymmetric linear combination can be formed from any product of one-electron wave functions in a fashion analogous to the one just described. This process is called "antisymmetrization" (*4*) and the particular linear combination is called an antisymmetrized product or determinantal wave function.

However, the simplification involved in using product wave functions is not enough to enable us to tackle the problem. We cannot in general find the best one-electron wave functions and in our choice of them we have to resort to further approximations. Two such methods have been in general use, both based on extensive use of physical intuition; the Heitler-London or valence bond method, and the molecular orbital method. Although these two approaches appear to be very different, the differences are not really profound, and they disappear completely if one proceeds with an actual calculation beyond the first few steps. In both methods it is customary (although not necessary) to use the so-called atomic orbitals as elementary building blocks for the construction of the one-electron wave functions. These are very closely related to the wave functions describing the possible states of the hydrogen atom (*5*). One reason for their use is the fact that they form an orthonormal set (*6*), i.e., they have the property that any arbitrary function can be expressed in terms of them to any desired degree of approximation. Atomic orbitals are not unique in this; there are many other sets of functions having this property. It is really immaterial which set of orthonormal functions we choose to approximate our one-electron wave functions, if only we take a sufficient number of them (which is generally very large). However, if we take only very few in order to make explicit calculations practicable, the choice of a set becomes important: A set whose very first members already give a relatively good approximation is clearly preferable. There is serious doubt whether from this point of view the set of atomic orbitals is really as advantageous as its almost universal use might suggest; indeed more recently, other "building blocks" (*7*) have been tried.

Very often we are primarily interested in calculating the lowest possible energy values of the system (ground state) and comparing these with the experimental values. We can then proceed as follows: We guess a wave function Ψ which is of the acceptable type and then evaluate the expression:

$$W = \frac{\int \ldots \int \Psi^* H \Psi d\tau_1 d\tau_2 \ldots . d\tau_n}{\int \ldots \int \Psi^* \Psi d\tau_1 d\tau_2 \ldots . d\tau_n}$$

where $d\tau_1$, $d\tau_2$, ..., $d\tau_n$ are volume elements in the coordinate space of electron 1,2, ... n. This is relatively easy to do. The remarkable fact is that the value of W so obtained is always higher than the true ground state energy of the system (*8*), and approaches it more closely the more the assumed wave function Ψ resembles the true wave function of the ground state in describing the actual charge distribution in the system. If we have a series of wave functions to try out, the one that gives the lowest value of W is therefore the best approximation.

The value of W obtained is actually quite insensitive to the form of Ψ and that means that even with very poor assumed wave functions one can get rather good energy values. The reverse side of the coin is of course that a "good" (i.e., close to experimental) value of W does not indicate that the wave function is close to the true one. Indeed, a quantitative calculation shows that the error in the approximate wave function is proportional to the square root of the error in the energy (*9*).

Exchange Forces: Mathematical Fictions

If we look at the expression for W more closely we find that we recognize a number of terms as simple coulombic energy terms corresponding to the attraction and repulsion of electrons and nuclei. However, usually terms constituting a large, or even major part of the total energy cannot be given such a simple interpretation. These are the terms which are often called "exchange energy" (*10*). It must be emphasized again that this does not in any way indicate the existence of new forces; they are only mathematical fictions which appear because of our poor choice of approximation wave functions and, in a sense, undo the damage to the energy caused by this choice.

That the division of the energy into separate terms is

artificial can be seen most easily by the following argument: One privilege we always have is to take the set of one-electron wave functions we have used and to form new linear combinations from these in any way we please. This leaves the form of the final wave functions and the value of the final energy completely unchanged. Mathematically, the whole process is trivial, but it does redistribute the energy, puts different amounts in the "exchange" terms and in the "coulombic" terms. This, of course, shows that the division of energy into "coulombic" and "exchange" terms depends only on the way the wave function happens to be written and is hence clearly devoid of any physical significance.

Minimizing Exchange Energy. A Physical Picture for Li_2

We might ask ourselves whether it is not possible to rearrange our starting approximation in such a way that almost all the energy appear as coulombic energy and the exchange energy be minimal. This indeed can usually be done. This is because the exchange energy is a measure of the overlap of the basic wave functions; hence if a set can be chosen which consists of functions which are essentially separate in space, our goal will be achieved. If this is done it has the great advantage that one can now look at the terms that are left and understand these in quite simple language, and one can begin to see in what way electrostatic forces only are holding the molecule together. A more technical and elaborate discussion of this point is to be found elsewhere (*11*).

In order to illustrate these ideas and procedures it is best to start out with a very simple case, not a coordination compound at all but a typical covalent bond. Most people in talking about the typical covalent bond start out with a hydrogen molecule. Unfortunately, the hydrogen molecule is far from being typical and for that reason it should be avoided. Let us take instead the lithium molecule, Li_2, which is still a reasonably simple system and yet has in it most of the essential features of chemical bond formation, and let us see how by the molecular orbital method one goes about the process of demonstrating its properties.

As we already mentioned, in almost all the work of this kind that has been done the starting points have been the atomic orbitals. The reason for this is the flexibility possessed by this set of functions; they are not actually present in lithium or any other molecule. As we shall see by the time we get through, practically all traces of these original functions have disappeared. One begins the process of molecular orbitals by putting together a number of these hydrogen-like orbitals to try to make orbitals suitable for the problem at hand. It turns out, for example, that it is desirable to put an orbital of the *s* type near each of the two lithium nuclei. It is then customary for reasons connected with symmetry to take these two functions, one around each nucleus and replace these two by their sum and their difference. In addition to these, one provides some further orbitals by the combination of other atomic wave functions. The variety of shapes and forms obtainable in this way is amazing. In other words, we begin our whole process by constructing from these building blocks some new pieces which are called molecular orbitals.

Electrons are now assigned to these orbitals in much the same way that we fill up the orbitals in an atom when we are considering the structure of the periodic table; that is to say, we put two electrons in each orbital, one electron of each of the two spins, beginning with the orbital of lowest energy until all the electrons have been assigned. In the present case of the lithium molecule there are six electrons in all, two each going into clouds concentrated around each nucleus and the last two going into a mixture of the 2*s* and 2*p* orbitals.

A good many of the popular descriptions stop at this point, indicating that this is how the electrons are distributed in the molecule. This unfortunately is misleading. When we have made our electron assignments we have essentially built a wave function for the entire molecule by multiplying together these various functions for the six electrons. And the product wave function obtained in this way cannot be used to describe the actual molecule because of the fact that it violates the Pauli exclusion principle, as explained above. It is now necessary to go through the process of antisymmetrizing the wave function, which is a process of some algebraic complexity and which completely destroys the identity of the electrons and also the shapes of the molecular orbitals with which we started.

After this antisymmetrizing process we have a function satisfying the Pauli exclusion principle but bearing very little resemblance to the original "building blocks." It is very difficult, if not impossible, to recognize the original atomic orbitals or even the secondary molecular orbitals which have been used in its construction, since very large and drastic changes occur during this antisymmetrization.

A symptom of these large changes is the exchange

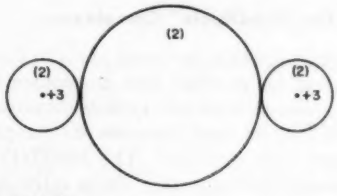


Figure 1. Li_2 molecule.

energy mentioned above. That is, if the energy is calculated, certain terms appear which can be interpreted as describing the coulombic interactions of the electrons in the original molecular orbitals. But other, very large, terms appear which cannot be interpreted physically (the exchange energy, referred to previously). If one now rearranges the starting molecular orbitals so as to minimize this exchange energy in the manner outlined before, one comes out with a picture which in schematic form is presented in Figure 1. Our set of functions consists now basically of just three parts. Two are the functions which are essentially the 1*s* function around the two lithium atoms; what is left is essentially a cloud located in between the two 1*s* orbitals with only minor fringes in other parts of space. There are two electrons in each one of the regions. Curiously enough, we began with two 1*s* functions. In the usual routine involving group theory these two are

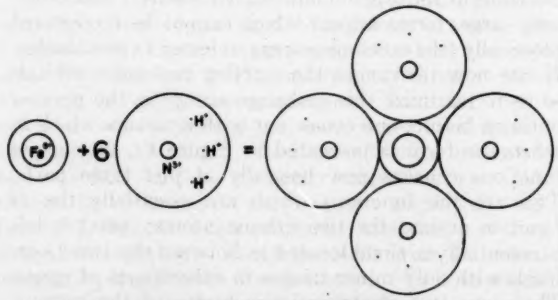
combined with each other. The process of eliminating exchange terms then undoes this process again and returns us right to where we started as far as those two orbitals are concerned.

The energy now consists simply of the following parts: First of all there is a certain kinetic energy for these electrons, which, because of the Heisenberg uncertainty principle, is related to the size of the clouds (the smaller the cloud, the larger the energy). And then the rest of the energy is simply the electrostatic interaction of the two +3 nuclei and the three clouds with a charge of −2 each. It is evident that this is equivalent to just two lithium ions with a pair of electrons in between; the whole thing is held together by the negative charge sandwiched between two positive charges, very similar to the arrangement one has in a sodium fluoride crystal. There are no mysterious forces acting at all. Of course, one has to consider not only what holds it together but also what opposes further shrinkage. The thing that prevents that is simply the kinetic energy. If the arrangement is compressed any further the increase in the kinetic energy of the electrons outweighs the lowering of the potential energy. The equilibrium separation is clearly the one at which the total energy has a minimum. The total energy is the sum of the kinetic energy, which is always positive (repulsive) and decreases with increasing internuclear distance, and the potential energy, which is always negative (attractive) and becomes less so with increasing internuclear separation. At the equilibrium point the total energy is negative (i.e., there is binding) and equal in magnitude and opposite in sign to the kinetic energy and equal to one half the potential energy. This follows from the virial theorem mentioned before.

This is all there is to the chemical bond in Li_2, and all other chemical bonds are extremely similar if the situation is analyzed to its logical conclusion.

The Picture for "Ion-Dipole" Complexes

One can apply exactly the same ideas to coordination compounds and see in what way a complex is held together. To take a common, typical example, we will take an iron(III) ion and examine its complexes with ammonia and with cyanide. The iron(III) ion itself consists basically of two parts. There is the center core, bearing a charge of +8, which is an argon-like structure with 18 electrons and the iron nucleus. Around this are five valence electrons which occupy a region with perfect spherical symmetry and with no signs of any



$Fe^{+3} + 6NH_3 = Fe(NH_3)_6^{+3}$

Figure 2. The formation of $Fe(NH_3)_6^{+3}$ ion from Fe^{+3} and NH_3. Only four of the NH_3 molecules are shown for reasons of clarity.

difference between directions at all. In this respect the ion is very much like an alkali ion but it differs from the latter in one very important respect: although we do have a spherical shell of valence electrons, it is incomplete since it is only half full. Therefore, more electrons can be inserted in it and that is basically what accounts for the difference between an alkali ion and one of a transition metal.

Let us suppose now that we bring up to this ion an ammonia molecule. The ammonia molecule again is nearly spherical; however, its electric charges have a lopsided distribution mainly because of the fact that we have the three hydrogen nuclei off center in the electron cloud. The ammonia molecule will then orient itself in such a way that the region nearest to the iron(III) ion is a region of negative charge whereas the other side has the positive charge to compensate it. In other words, we have here essentially a dipole arrangement, but the distances are so small that if one attempts to calculate energies by using the dipole moment one is making a very bad error. However, because of the fact that the ammonia molecule is turned with its negative side toward the positive ion there certainly is an attraction, a simple electrostatic attraction, between the two molecules and this causes the ammonia to move inward until it gets to the point where it touches the outer shell of valence electrons in the ion.

Now, however, comes a very basic question. Will it go any further? It is possible for the ammonia to push right in until its electron clouds are in contact with the central core of the iron(III) ion. There is a strong electrical force tending to pull the ammonia molecule in. The reason that this does not happen is the fact that we are not dealing with just one ammonia, but with as many as can crowd around the central ion, and that number is six. The inward forces on these ammonias are acting on all six of them; they are all being driven in toward the center. However, in order to accommodate them closer to the inner core, the five electrons that were already occupying the space have to go somewhere else. In other words, these electrons have to be moved from an energetically favorable position right next to a +8 charge out to some distance from that. And apparently in the case of the iron(III)-ammonia complex the energy required to move out the electrons is more than that which can be gained by pulling the ammonias in. As a result, the ammonias do not approach more closely than the fringes of the central ion electron shell and form what is commonly called the ion-dipole type of bond. This is represented schematically in Figure 2 on which, however, only four of the six ammonia molecules surrounding the central ion are shown. The other two are to be thought of as situated vertically above and below the central ion.

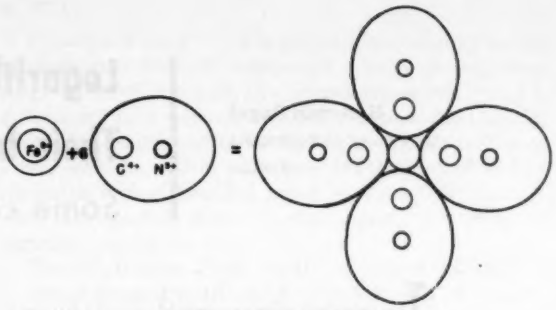
The Picture for "Covalent" Complexes

Let us now contrast the situation in the ammonia case with what happens if we bring in cyanide ions instead. The cyanide group has two atoms, a carbon and a nitrogen. These two are held together by a triple bond, which means simply that there are three pairs of electrons shared between the two atoms (which are still held together by electrostatic forces only). We can again bring up six of these cyanides until they have just

reached the surface of the valence electron shell of the Fe^{+3}. Again, there is the same force as there was with the ammonia pulling them in toward the center. It is somewhat greater in fact because the cyanide ion has a negative charge. However, this difference is not at all important: for example, the fluoride ion, which has a negative charge, does not get pulled in. But now there is one rather important difference which arises primarily from the fact that the carbon has a triple bond connecting it to the nitrogen. This means that six of the electrons around the carbon are pulled off toward the nitrogen atom leaving, as it were, the central +4 core of the carbon atom somewhat exposed. Let us now consider an electron displaced out of the valence shell of the Fe^{+3} ion as the cyanides come in. Such an electron can get into a region in which it is, although farther away from the iron nucleus, now quite close to the carbon nucleus. In other words, it can get back some of the energy it loses in being forced away from the iron by attraction to the carbon nucleus. This difference is apparently large enough in the cyanide case so that these cyanides are driven all the way in until they to all intents and purposes touch the central core. This is represented schematically in Figure 3 on which, however, only four of the six cyanide groups surrounding the central ion are shown. The other two are to be thought of as situated vertically above and below the central ion.

This type of bonding is usually referred to as covalent and often described not in direct electrostatic terms, as we have done here, but in terms of resonance; in this case resonance with states in which there are double bonds between the iron and carbon and between the carbon and nitrogen. Conversely, an ionic bond can also be described in covalent terms; for instance, in the case of the ferric ion-ammonia complex we can construct molecular orbitals using the 4*s*, 4*p*, and 4*d* orbitals of the iron and put into these the unshared electron pairs of the ammonia, combine them into octahedral hybrids and come out with a perfectly satisfactory picture of the compound.

These are simply different ways of saying the same thing, not different explanations. As was pointed out before, all binding is basically and exclusively electrostatic in nature; the difference between those bonds that are commonly called "ionic" and those that are commonly called "covalent" is simply that in the former case the binding can be expressed in terms of the electrostatic interactions of the constituent ions or atom groups, considered as essentiallly undeformed charged spheres or dipoles, while in the latter case the charge distributions holding the compound together are very different from those in the constituent parts.



$Fe^{+3} + 6CN^- = Fe(CN)_6^{-3}$

Figure 3. The formation of $Fe(CN)_6^{-3}$ ion from Fe^{+3} and CN^-. Only four of six cyanide groups are shown for reasons of clarity.

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"I can take a group of young people and teach them to be inventors, if I can get them to throw off the hazard of being afraid to fail. . .the more education a man has the less likely he is to be an inventor. This is because, throughout his life he has been taught the danger of failure. From the time he enters the first grade until he graduates from the university he is examined three or four times each year and if he fails he is out and in many cases disgraced. In research and invention work you fail hundreds and even thousands of times and if you succeed once you are in.

. . .The educated person must be taught that it is not a disgrace to fail and that he must analyze every failure to find its cause. (He) must learn to fail intelligently. . . . For failing is one of the greatest arts in the world."

C. F. Kettering

H. Armin Pagel
University of Nebraska
Lincoln

Logarithms, Exponentials, and Their Integrations

Some calculus for chemists

The solution of many problems in physical chemistry depends on various mathematical relationships among the properties of the base e of the natural logarithm system. Students may have developed these fundamental relationships in a previous course in the calculus. Nevertheless, they frequently have no definite idea as to how the mathematical operation actually is related to the physical or chemical process being considered. This can be illustrated by solving a simple problem of light absorption (Lambert's law) in the conventional manner. Using the data: $I_0 = 100$ (%), as the intensity of the incident light; $l = 1$ cm, as the length of solution traversed by the light; $k = 1$. Calculate I_t, the per cent of incident light transmitted.

$$\begin{aligned}
\int_{I_0}^{I_t} dI/I &= -k\,dl \\
\int_{I_0}^{I_t} dI/I &= -k \int_{l=0}^{l=1} dl \\
\ln I_t/\ln I_o &= -kl \\
\ln I_t &= \ln I_o - kl \\
I_t &= e^{(4.606-1)} \\
&= e^{3.606} = 36.8\ (\%)
\end{aligned}$$

Although students know that both the light absorption and the integration are continuous processes, they seem unable to grasp exactly how the two processes operate simultaneously to yield a definite numerical answer. We shall return to this illustration later.

The logarithm base e is defined as

$$e = \lim_{n \to \infty} (1 + 1/n)^n$$

Since it is impossible even to write a number large enough to represent infinity, this expression at first appears to be quite meaningless. But by the method of the calculus, using the binomial theorem and theorems of limits, it takes the form of the infinite series:

$$e = 1 + 1 + 1/2! + 1/3! \ldots = 2.71828\ldots$$

However, the special significance of e as a logarithm base is still not clear. Some textbooks show that calculations of $(1 + 1/n)^n$ for increasing values of n give increasing numerical values which approach closer and closer to 2.71828... For example where n is 1, 5, 100, and 10,000, the values increase 2.000, 2.489, 2.717, and 2.718, respectively. As n approaches infinity, the value approximates e.

Daniels[1] has given an excellent discussion for physical chemistry students, showing that the evaluation of the base e as indicated above is related to the "compound interest law." In turn, he has given several examples to show how the compound interest (or exponential growth) law is useful for gaining a better understanding of chemical processes which involve the mass action law.

Comparison of the evaluation of the base e to the compound interest law does not, however, show how the numerical value 1 at e^0 increases to 2.71828... at e^1. This must be considered in detail before starting the discussion of the topics indicated in the title of this paper.

If we fix our attention on a given value of n in $(1 + 1/n)^n$, for example where $(1 + 1/5)^5 = 2.48832$, the numerical increase (starting with $(1 + 1/5)$ becomes obvious if the calculation is performed in a certain manner. If calculated as a power, namely $(6/5)^5$, or by means of the binomial theorem which gives $1 + 5/5 + 10/25 + 10/125 + 5/625 + 1/3125$, the progressive increase is not apparent. But if calculated by repeated multiplication, $(1 + 1/5)(1 + 1/5)\ldots$, the numerical values increase stepwise, 1.2; 1.44; 1.728; 2.0736; 2.48832. Each time we multiply by $(1 + 1/5)$ the numerical value always increases by 1/5th of the immediately preceding value, as is easily seen from: 1.2 + (1/5 of 1.2) = 1.44; 1.44 + (1/5 of 1.44) = 1.728, etc. This expresses the compound interest or exponential growth law, where the rate of change, $(1/n)$, is constant while the actual numerical change is always $1/n$th of the quantity present at any stage of the process.

The same principle can be applied to visualize how the numerical value 1 increases to 2.71828..., as e^0 increases to e^1. We start with

$$\lim_{n \to \infty} (1 + 1/n)^1 = 1 = e^0.$$

As n approaches infinity the value of $1/n$ will always continue to be larger than zero. Therefore we can imagine that each time we multiply by $(1 + 1/n)$, the numerical value will always increase by the very small amount of $1/n$th of the immediately preceding value. If the process of multiplying $(1 + 1/n)$ by itself were repeated $(n - 1)$ times, or "to the total of n factors," the value would finally reach 2.71828..., which approximates e^1.

(The manner in which the exponent of e progressively increases during the "repeated multiplication" process is given later.)

Numerical values larger than 2.71828...may be expressed as the limit of

$$\lim_{n \to \infty} (1 + 1/n)^{xn} = e^x,$$

where x is any positive value larger than 1. By the method of the calculus this takes the form $e^x = 1 + x + x^2/2! + x^3/3! \ldots$. The numerical increase from

[1] DANIELS, FARRINGTON, "Mathematical Preparation for Physical Chemistry," (Chap. 12). McGraw-Hill Book Co., New York, 1928.

e^0 to e^x may now also be visualized by repeated multiplication of $(1 + 1/n)$:

$$e^x = \lim (1 + 1/n)^{xn}, \text{ as } n \to \infty$$
$$= \lim (1 + 1/n)^n(1 + 1/n)^n \ldots (1 + 1/n)^n, \text{ to } x \text{ factors}$$
$$= \lim (1 + 1/n)(1 + 1/n) \ldots (1 + 1/n), \text{ to } xn \text{ factors}$$

It is obvious that the latter expression could never actually be performed as indicated. Nevertheless, one can visualize that as x increases without limit, the numerical increase from e^0 to e^x proceeds continuously from 1 to infinity according to the compound interest or exponential growth law. Using the same concept, one also proceeds from e^0 to e^{-x} for values less than one, where $(1 - 1/n)^{xn}$ expresses the continuous decrease from 1 to zero as the limit.

The demonstrations to be given are based on numerical approximation methods. The number of decimals carried is generally necessary to maintain a simplified system, even though some arithmetical inconsistencies will occur as a result. The symbol $\doteq$ will be used to indicate "approximately equals."

If we assign the value 10,000 for n in $(1 + 1/n)^n$ and solve (using 10 place logarithm tables), we find that $(1 + 1/10{,}000)^{1.0000} = 2.71814\ldots$. This value differs from 2.71828. . .by only about 5 parts per 100,000, therefore 2.718. . . will be used (for brevity) *as though it were* $e^{1.0000}$.

By repeated multiplication of $(1 + 1/10{,}000)(1 + 1/10{,}000)\ldots$, the numerical value, starting at approximately 1, will increase, according to the compound interest concept, to any desired large value. In this manner (using logarithms for computation) one can obtain a set of selected values which will serve as the basis for all of the discussions to follow.

The approximate numerical value and the equivalent as an exponential are given below each term. (The arrows merely indicate the direction of increasing values.)

$a^0 = 1$

The expression $a^0 = 1$ is derived very simply by the fundamental laws of exponents. Such presentation tends to leave one with the impression that $a^0 = 1$ is an isolated fact, because it does not show the path by which, for example a^m proceeds to a^0. As demonstrated above, any logarithm base may be thought of as any numerical value obtained by $(1 + 1/n)(1 + 1/n)\ldots$ This concept will serve to give a more complete interpretation of $a^0 = 1$.

The fifth term in Table 1 is $10^1 = (1 + 1/10{,}000)^{23{,}026}$ or stated generally, $10^1 = (1 + 1/n)^{xn}$. By *repeatedly* taking roots to a total of xn, the value progressively decreases to $(10)^{1/xn} = (1 + 1/n)^1$. If n is allowed to approach infinity, the limiting values become $10^0 = 1$. The same reasoning holds for *any* base, because in taking the same number of roots corresponding to the exponent of $(1 + 1/n)$ for any particular base, "a," one always arrives at the starting point, $(1 + 1/n)^1$, where the limiting value is always $a^0 = 1$.

One can illustrate and also extend the application of this concept by considering a unimolecular chemical reaction: Starting with 2 units of substance, designated as a^m, this quantity will decrease exponentially to $a^0 = 1$. As the reaction continues beyond this point, the quantity remaining becomes less than 1 and the exponent of "a" becomes negative. Therefore one ought to think of $a^0 = 1$ as a *transition* point lying between the limits of the continuously changing value from a^x as infinity, to a^{-x} as zero.

Relation of the Exponent of $(1 + 1/10{,}000)^{10{,}000}$ to $e^{1.0000}$

During the repeated multiplication process, the exponents of $(1 + 1/10{,}000)^1$ add, therefore the exponent 10,000 must here be thought of as the accumulation of 10,000 separate exponents, each having the value 1.

Table 1

$\left(1 + \frac{1}{10{,}000}\right)^1 \rightarrow$	$\left(1 + \frac{1}{10{,}000}\right)^{6{,}932} \rightarrow$	$\left(1 + \frac{1}{10{,}000}\right)^{10{,}000} \rightarrow$	$\left(1 + \frac{1}{10{,}000}\right)^{10{,}001} \rightarrow$	$\left(1 + \frac{1}{10{,}000}\right)^{23{,}026} \rightarrow \ldots$
$= 1.0001$	$\doteq 2^{1.0000}$	$= 2.718\ldots$	$= 2.718\ldots$	$\doteq e^{2.3026}$
$\doteq e^{0.0001}$	$\doteq e^{0.6925}$	$\doteq e^{1.0000}$	$+ 0.0002718\ldots$	$\doteq 10^{1.0000}$
$\doteq a^0$	$\doteq 10^{0.3010}$	$\doteq 10^{0.4343}$	$\doteq e^{1.0001}$	

The separate topics to be discussed now are important because they must be applied for visualizing logarithm tables and integrations.

The Origin of Various Logarithm Bases

Any numerical value occurring among the ever increasing values of $(1 + 1/10{,}000)(1 + 1/10{,}000)\ldots$ could be chosen as a logarithm base. For example in Table 1 above, the base 2 starts as 2^1 at the second term where the exponent of $(1 + 1/10{,}000)$ is 6,932. As the repeated multiplication continues until the exponent of $(1 + 1/10{,}000)$ has doubled, (at 13,864), the numerical value would reach 4, namely 2^2; when the exponent has tripled the value is 8, or 2^3. Also, since 2^3 is 8^1, this would be the starting point for the base 8. The base 5 would start at the exponent 16,094. As indicated in the third term of Table 1, e^1 is at the exponent 10,000; e^2 will be at 20,000, etc.[2]

Now, since this exponent 10,000 corresponds to 1.0000 as the exponent of $e^{1.0000}$, we see that this 1.0000 is also composed of 10,000 separate logarithm increments or units, where each $\Delta\ln$ has very nearly[2] the value 0.0001. The important observation is: Each time we multiply by $(1 + 1/10{,}000)$, the logarithm increases nearly 0.0001, while the numerical value increases 1/10,000th of the immediately preceding value, according to the compound interest concept. (This is shown specifically by going from the third to the fourth term.) The relation of the exponent of $(1 + 1/10{,}000)$ to the exponent of e for any term in Table 1

[2] It should be noted that the above statements are rather close approximations. Higher accuracy would result if, instead of using $(1 + 1/10{,}000)$ as the repeating multiplier, one used $(1 + 1/100{,}000)$, whereby, for example e^1 becomes $(1 + 1/100{,}000)^{100{,}000}$. By using ever increasing values until the multiplier becomes $(1 + 1/n)$, $n \to \infty$, the statements given here and elsewhere would become more and more accurate.

follows the same reasoning. For example, in the second term the exponent of e consists of 6,932 separate $\Delta\ln$ units, each being 0.0001.

$de^x = e^x dx$

In the calculus this is derived by differentiating the infinite series which represents e^x (shown previously). The complete statement of this problem is: If $y = e^x$, show that $dy = e^x dx$. This is easily explained since it follows the compound interest concept where the numerical increase Δy equals the rate, ($\Delta x \doteq 1/n$), times the quantity present, ($y = e^x$), at that stage. The choice of y may be any numerical value along numerical increase of $(1 + 1/10{,}000)(1 + 1/10{,}000)\ldots(1 + 1/10{,}000)$, >1 to infinity factors, where any specified value of y will have a definite value of e^x. Such value of y is shown in the third term of Table 1 and y' in the fourth.[2]

$$\begin{aligned} y &= (1 + 1/10{,}000)^{10{,}000} \\ &= e^x \doteq e^{1.000} = 2.718\ldots \\ y' &= (1 + 1/10{,}000)^{10{,}001} \\ &= e^{(x+\Delta x)} \doteq e^{1.0001} = 2.718\ldots + 0.0002718\ldots \\ \Delta y &= y' - y = 0.0002718\ldots \\ \Delta y &\doteq e^x \Delta x \\ &\doteq (2.718\ldots)(0.0001) \doteq 0.0002718\ldots \end{aligned}$$

To visualize the above solution we use concepts from the previous section. The sequence of reasoning becomes: The increase of $e^{1.0000}$ to $e^{1.0001}$ (namely $\Delta x \doteq 0.0001$), represents an increase of 1 in the exponent of $(1 + 1/10{,}000)$, from 10,000 to 10,001, which will increase the numerical value by 1/10,000th of the present value. But the present value is $y = 2.718\ldots$, hence the increase, *which is* Δy, is simply $2.718\ldots$ times 1/10,000. Instead of using these particular values for y and y', the same explanation will be maintained by setting up any two consecutive terms so that the exponent differs by 1. For example, $(1 + 1/10{,}000)^{6{,}932}$ and $(1 + 1/10{,}000)^{6{,}933}$. (See the second term in Table 1.) The same reasoning would hold if the exponents differed by 2 (or more), but the accuracy would decrease because "the simple interest for two days is not quite the same as the compound interest for two separate days."

$d(a)^x = \ln(a)(a)^x dx$

The fifth term of Table 1 indicates that $(1 + 1/10{,}000)^{23{,}026}$ equals either $e^{2.3026}$ or $10^{1.0000}$. The exponents of e consists of 23,026 separate $\Delta\ln$ increments (each being 0.0001), while the exponent 1.0000 of the base 10 consists of 10,000 separate $\Delta\log_{10}$ increments, each also being 0.0001. Therefore each $\Delta\log_{10}$ corresponds to approximately 2.3 $\Delta\ln$ increments. Since each $\Delta\ln$ increment (namely 0.0001) increases the numerical value by 1/10,000th of the total, therefore each $\Delta\log_{10}$ increment (0.0001) will increase the numerical value about 2.3 times as much. This is like saying that the simple interest on \$10 at 2.3/10,000 interest rate, if computed once in 2.3 days, is about the same as the compound interest on \$10 at 1/10,000 interest rate if computed each day for 2.3 days. More specifically, \$10 would increase to $\$10(1 + 2.3/10{,}000)^1$ in the first instance, which is nearly[2] the same as $\$10(1 + 1/10{,}000)^{2.3}$. Thus one sees why for a given exponent increment, for instance from $10^{1.0000}$ to $10^{1.0001}$, the numerical value increases 2.303 times as much as it does for the same exponent increase from $e^{1.0000}$ to $e^{1.0001}$. Stated mathematically,

$$\begin{aligned} d(10)^x &= \ln(10)(10)^x dx \\ &= 2.303\,(10)^x dx \end{aligned}$$

This discussion suggests the relation of the $\log_{10}$ and $\log_e$ tables, discussed later.

$d\ln x = dx/x$

This equation states that the *actual* logarithm change is equal to the *relative* numerical change. This also says that the ratio of the numerical increase to the quantity present equals the rate. This fact is easily visualized by using the third and fourth terms of Table 1 and the discussion presented above. (The ("third term")(1 + 1/10,000) equals the ("fourth term").)

$$\begin{aligned} x &= 2.718\ldots \text{ (third term)} \\ \Delta x &= 0.0002718\ldots \text{ (fourth term)} \\ \Delta\ln x &\doteq \ln\left[e^{(1.0001\ -\ 1.0000)}\right] \doteq 0.0001 \end{aligned}$$

It must now be stated that the actual logarithm change[3] for a relative change of 1/10,000, (namely $\Delta x/x$), is $0.000099995\ldots$, instead of 0.0001. Therefore,

$$\begin{aligned} (d\ln x = dx/x) \\ \Delta\ln x &\doteq \Delta x/x \\ 0.000099995\ldots &\doteq 0.0002718\ldots/2.718\ldots \\ 0.000099995\ldots &\doteq 0.0001 \end{aligned}$$

This solution does not exactly satisfy $d\ln x = dx/x$, but if one had used the multiplier $(1 + 1/n)$, $n \to \infty$ in setting up Table 1, the above reasoning would be exactly the same and one would arrive at $d\ln x = dx/x$.

Logarithm Tables and Integration

Although $\log_e$ tables look complicated, they are really simple because the numerical values increase $(1 + 1/n)(1 + 1/n)\ldots$, while the logarithms change as shown above. To clearly visualize this we use $\Delta\ln x \doteq \Delta x/x$ and choose a *constant* value for $\Delta\ln x$, for example 0.0001 (actually $0.000099995\ldots$), whereby $\Delta x/x$ must also remain constant. Now as x increases, Δx must also increase in the same proportion as does x. For example, for the following pairs of numbers which differ by 1 part/10,000 (relative), $\Delta\ln x$ is always the same ($0.000099995\ldots$): (1.0000, 1.0001); (3.0000, 3.0003); (8.0000, 8.0008); (10.000, 10.001). Therefore the construction of "natural" log tables follows the compound interest or exponential growth law, where the rate, $\Delta\ln x$, may be considered constant while the numerical change, Δx, always depends on how large x is at any stage.

Using this concept we can now visualize the integration given in the introduction. Starting with $dI/I = -k\,dl = (-1)dl$ we will arbitrarily subdivide $l = 1$ cm into 10,000 separate Δls, each having the value 0.0001 cm. Since Δl is chosen as 0.0001, this fixes the *ratio*

[3] Some values showing the changing numerical relation between $\Delta x/x$ and $\Delta\ln x$ are tabulated below.

$\Delta x/x$	$\Delta\ln x$
$1/10^4$	$0.0_9 9_5 1_0 3_4\ldots$ [a]
$1/10^5$	$0.0_9 9_5 1_0 3_5\ldots$
$1/10^6$	$0.0_9 9_5 1_0 3_6\ldots$
.	.
.	.
$1/10^{11}$	$0.0_{11} 9_{11} 5_{11} 0_{12}\ldots$

Here $\Delta\ln x$ approaches closer and closer to $\Delta x/x$.

[a] The subscripts indicate the number of identical repeated figures. Thus, $0.0_9 9_5 1_0 3_4$ means 0.0000999950003333.

$\Delta I/I$ *constant* as 0.0001. Since $\Delta \ln I \doteq \Delta I/I$, then $\Delta \ln I$ will also have nearly[3] the same constant value, (actually 0.000099995. . instead of 0.0001). Now as the light passes through *each* Δl the intensity, I, always decreases 1/10,000th of the immediate total, and *simultaneously*, $\ln I$ will also always decrease by the value of $\Delta \ln I$, (0.000099995. . .). Starting with $I_o = 100 = e^{4.606}$, the intensity decreases 100.00, 99.99, 99.98. . ., 99.97. . ., etc. When the light has passed through the 10,000 Δls, the remaining light, I_t, = 36.8%. During this process the 10,000 separate $\Delta \ln I$ increments have added up to 10,000 × 0.000099995. . . = 0.99995. . ., or essentially 1.

$$\text{Therefore } I_t = e^{(4.606-1)} = e^{3.606} = 36.8\%$$

Therefore we now see clearly that the continuous mathematical operation exactly describes the continuous physical process!

Since $d\log_{10}x = 0.4343\ dx/x$, the $\log_{10}$ tables do not express the simplest relation between log and number change. This is one reason why the base e has special significance and may be thought of as "natural" since no other base can give the simple relation $d\log_e x = dx/x$. The same kind of simplicity is evident in $de^x = e^x dx$.

Integration of Work Under the pv Curve

For this demonstration we will calculate the work done when 1 mole of an ideal gas is allowed to expand isothermally and reversibly from 2 liters to 10 liters at 273°K.

The work, w, is shown by the calculus to be the area under the pv curve between the limits of 2 and 10 liters, as shown in Figure 1:

$$dw = pdv = RT\ dv/v = RT\ d\ln v$$
$$w = RT \int_2^{10} dv/v = RT \int_2^{10} d\ln v$$
$$= RT \ln 5$$
$$= 1.6094\ RT$$

If we think of expanding the gas according to the compound interest law, then the expansion will exactly follow the process indicated in Table 1, where 16,094, (namely from the exponent 6,932 to 23,026), separate expansion steps take place to increase the volume from 2 to 10 liters. Each successive volume, v, will always be 1/10,000th (of the total) larger than the previous v, therefore the *ratio* $\Delta v/v$ will be *constant*, namely 1/10,000. (The positions of three of the 16,094 constant ratio $\Delta v/v$ values are shown in Fig. 1.)

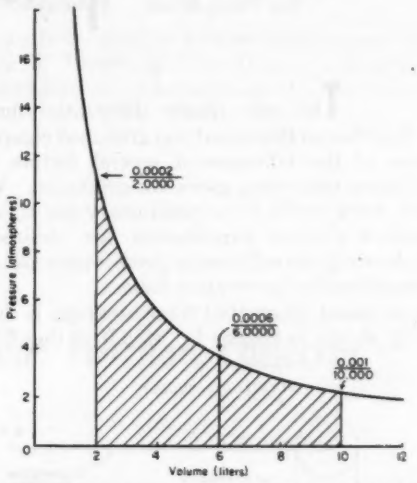


Figure 1. The shaded area under the curve is the work done. Also shown are the locations of three of the 16,094 constant ratio $\Delta v/v$ values, which correspond to constant value Δw, $p\Delta v$, $RT\Delta v/v$, and $RT\Delta \ln v$ work increments.

Referring to $dw = pdv = RTdv/v = RTd\ln v$, the 16,094 expansion steps represent 16,094 separate equivalent terms Δw, $p\Delta v$, $RT\Delta v/v$ and $RT\Delta \ln v$. For $\Delta v/v = 1/10{,}000$ (constant), $\Delta \ln v = 0.000099995\ldots$ (constant). Now Δw, (or $p\Delta v$), $= RT\Delta \ln v = (0.0000\text{-}99995\ldots)RT$ (constant). Therefore as the gas is expanded stepwise through the 16,094 steps, the integration *simultaneously* adds the 16,094 constant value Δw increments:

$$w = (16{,}094)\Delta \ln v RT$$
$$= (16{,}094)(0.000099995\ldots)RT \doteq 1.6094\ RT$$

Division of **CHEMICAL EDUCATION**

American Chemical Society

Nominations for Office of Member-at-large of the Executive Committee, 1959–60

Richard W. Ramette, Associate Professor, Carleton College, received his B.A. from Wesleyan. In 1954 he received the Ph.D. in analytical chemistry at Minnesota and immediately joined the faculty at Carleton. His research interests are in the field of aqueous solution equilibria and thermodynamics. His teaching interests deal with the problem of improving the presentation of undergraduate analytical chemistry through the increased introduction of "research-like" experiments. The NSF awarded him a Science Faculty Fellowship to further this approach. He has served for three years as secretary-treasurer of the MACTLAC and currently is on the Visiting Scientist program of the Division. He also is director of a summer conference for college teachers on "Recent Advances in Analytical Chemistry."

Harry W. Walborsky, Associate Professor, Florida State University, has provided imaginative leadership in attracting good students into chemistry as a career. The Florida State University Summer Science Camp which he helped to establish has served as a model for nationwide attention. Born in Lodz, Poland, educated in New York City, he obtained the B.S. from CCNY and the Ph.D. degree from Ohio State. Awarded a USPH post-doctoral fellowship, Dr. Walborsky studied for a year at the Institute for Organic Chemistry, Basle, Switzerland. He was also a research associate at Cal Tech and at UCLA before coming to Tallahassee in 1950. He has published over 30 papers in the area of bridged-bicyclic systems, cyclopropanes and fluorinated amino acids.

Walter Borzani
and **Marina L. R. Vairo**
Escola Politecnica,
University of Sao Paulo
Sao Paulo, Brazil

A Simple Differential Fermentograph

The very simple differential fermentograph described in this report can give good comparative measures of the influence of several factors on the fermentation rate when gases are produced. When a research work is still in its preliminary phase, or when demonstrative class experiments are desired, this simple device gives sufficiently precise information and saves considerable observation time.

The proposed differential fermentograph is diagrammatically shown in Figure 1. If ΔM is the difference

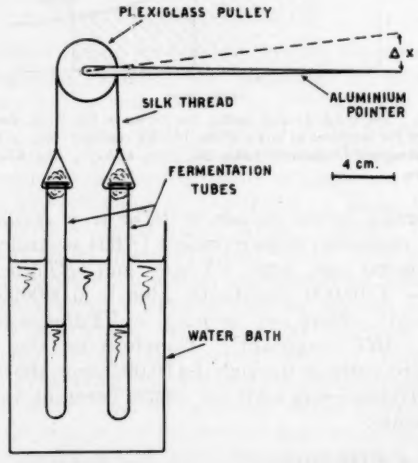


Figure 1. Differential fermentograph.

of the weight losses of the fermentation tubes, the displacement ΔX of the pointer extremity will be:

$$\Delta X = K\Delta M \qquad (1)$$

where K is a function of the fermentation tube diameters, the density of water (consequently of the temperature), the pulley diameter, and the pointer length. This theoretical equation represents with good accuracy, the experimental relation between ΔM and ΔX (Fig. 2) obtained with the fermentograph represented in Figure 1. Variations in the density of water in response to temperature changes as great at 10°C practically do not influence the equilibrium of the system.

A water level variation h in the bath will cause a displacement ΔX of the extremity of the pointer given by:

$$\Delta X = \frac{L}{R}\frac{n-1}{n+1}h \qquad (2)$$

where L is the pointer length, R is the pulley radius, and n is the ratio of the cross-section areas of the

This work was supported in part by grants-in-aid from the Brazilian National Research Council.

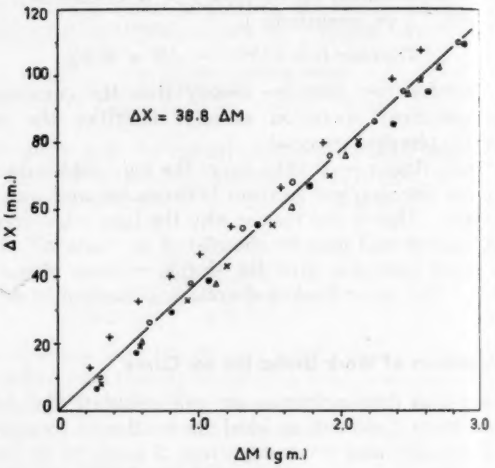


Figure 2. Fermentograph's calibration curve.

fermentation tubes. Equation (2) shows that when the fermentation tubes have the same diameter ($n = 1$), the water level variation in the bath does not influence the system. If the cross-section areas of the fermentation tubes are not identical, equation (2) permits the calculations of the maximum water level displacement in the bath that causes a given maximum displacement of the pointer extremity. Otherwise, as the temperature has little effect on the equilibrium of the system, the simple water bath represented in Figure 1 can be substituted by a constant level water bath.

The apparatus can be operated in the following way: The fermentation tubes, with the solutions to be studied, are suspended from the pulley and are im-

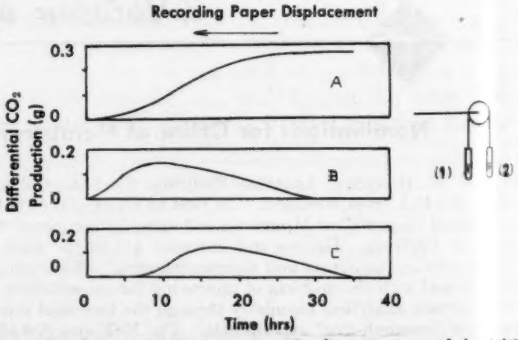


Figure 3. Curves obtained in alcoholic fermentations of backstrap molasses. Approximate initial sugar concentration = 140 g/l. Volumes of solutions in tubes (1) and (2) = 5 ml. Curve A: Tube (1) contained 10 g/l of pressed yeast, tube (2), none. Curve B: Tube (1) contained 100 g/l yeast, tube (2), 10 g/l. Curve C: Both tubes contained 10 g/l of yeast; pH of tube (1) = 5.5, pH of tube (2) = 2.5.

mersed in the water bath at a given temperature; 1 to 2 ml of liquid vaseline can be used in each tube in order to reduce evaporation losses. To avoid a considerable reduction of the fermentograph sensibility, the extremity of the pointer does not touch the recording band; it only makes light signals in narrow strips (about 1 mm width) of solid vaseline stained with methylene blue, equally distributed on the recording paper and parallel to the axis of the clockwork-driven drum.

Figure 3 shows the curves obtained with the differential fermentograph in some alcoholic fermentations of sugar cane molasses. Curve *A*, obtained with only tube No. 1 inoculated, is a normal CO_2 production curve; curves *B* and *C*, obtained with both tubes inoculated but in different fermentation conditions, show that the fermentation rate in tube No. 1 is greater than in tube No. 2 but that in both tubes the fermentation is complete.

Acknowledgment

The authors wish to express their appreciation to Joaquim J. Pereira and to Helio P. Engelberg for their assistance in the fermentograph construction.

B. A. Parkin
and **G. W. Hedrick**
U. S. Department of Agriculture
Olustee, Florida[1]

Chromatographic Fraction Collector

The frequent need for chromatographic analyses of reaction products prompted the construction of a fraction collector which would take up to sixty samples. A collector, Figure 1, entirely automatic and mechanical in operation, based on a tipping siphon was constructed. Although most of the individual construction features have been employed in fraction collectors previously described,[2] the combination used by the authors has resulted in an apparatus low in cost and simple to build and operate.

In operation, the chromatographic column is placed over the center of the instrument where the eluent drops into the siphon drip cup (*A*), and runs to the siphon through the connecting tube. As the siphon begins to load, it tips down, disengaging the lower pin of the swing stop (*Q*) from the square screw hook (*S*). The siphon swings to the next position where the upper pin of the swing stop engages the screw hook stopping the siphon discharge tube over the sample receiver (*T*) held in the circular rack. In this position the siphon loads completely and discharges. After discharge the siphon tips up, the upper swing stop pin clears the screw hook, and the lower one engages it. The cycle then repeats with the siphon swinging to the next position when it tips down after being partially loaded with the next sample.

The siphon design shown provides for a small surface area at the discharge level thus reducing errors caused by differences of liquid head at discharge resulting from droplets hanging in the discharge tube. The siphon is also made adjustable by insertion of a glass tube through an airtight rubber sleeve on the tube at the top of the siphon bulb. Raising or lowering the tube varies the volume of air trapped in the bulb and thus the final volume of eluent at discharge. A change in fraction size may necessitate adjustment of the counterbalance weight (*E*). The siphon is fastened firmly in the body of its holder by means of a paper bushing around the drip cup. The siphon tips with its holder on 60° knife edges (*C*) set in the 90° V bearings (*F*) and the entire carrier and siphon rotate on the point of the swing pivot post (*P*) bearing in a smooth depression in the bottom of the tip pivot support (*K*). The heavy plate at the bottom of the siphon carrier lowers the center of gravity and eliminates binding on the swing pivot post when the siphon loads. The swing pivot post is made of $^1/_8$-inch steel rod machined or carefully hand-shaped to a smooth 30° point and

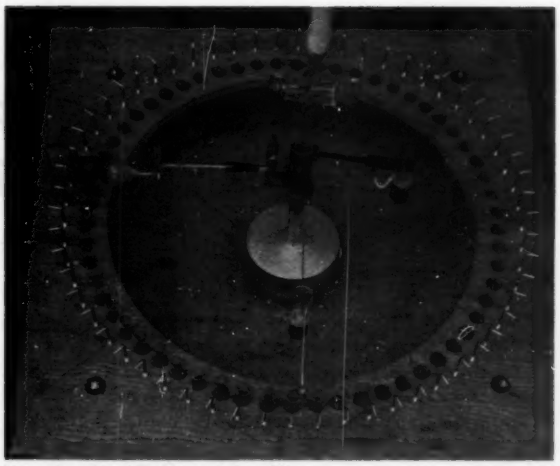


Figure 1. Fraction collector assembly.

[1] Naval Stores Research Station, one of the laboratories of the Southern Utilization Research and Development Division, Agricultural Research Service, U.S. Department of Agriculture.

[2] James, A. T., Martin, A. J. P., and Randall, S. S., *Biochem. J.*, **49**, 293 (1951); Dupuy, P., and Morcau, C., *Bull. soc. chim. France*, **1957**, 521.

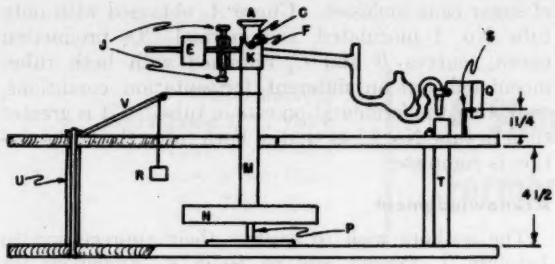


Figure 2. Receiver rack with syphon and carrier in place.

welded or threaded and fastened with nuts top and bottom into a steel plate which is screwed to the instrument base. Rotational force is supplied by a weight (R) attached to a string wound around the $^3/_8$-inch pipe (M) one or two turns and leading over a smooth steel rod (V) situated high enough that the weight does not come to rest on the receiver rack before it completes its travel. The swing stop is fashioned from $^1/_8$-inch bronze welding rod and fastened to the siphon with a rubber padded hose clamp. The receiver rack is made of half-inch plywood. The upper board has a 15-inch diameter hole cut from the center. The $^3/_4$-inch holes which hold the 18 × 150-mm rimless test tube receivers, are spaced at 6° intervals on a circle of $9^1/_2$-inch radius and are drilled about $^1/_4$-inch deep in the lower board. The rack is assembled with suitable pipe separators (U) and six-inch stove bolts. The square screw hooks used are commercially available with short threaded sections on the long ends. These are screwed into the rack on a line through the center of the tube hole and the center of the rack where it crosses a circle having a radius of $10^1/_2$ inches.

The apparatus is assembled as shown and adjustments are made in the counterbalance, turn or swing weight, tipping adjustment screws (J), and swing stop until smooth operation is obtained. Final individual adjustment of the siphon position over each tube may be made by turning the screw hooks in the rack.

The authors wish to thank their co-workers for their many helpful suggestions and especially R. A. Tyre and H. R. Lanier who constructed the apparatus.

Luis M. Borrero
Facultad de Medicina,
Universidad del Valle
Cali, Colombia, South America

An Experiment on Osmotic Flow

This paper describes a procedure for the semiquantitative study of osmotic flow. A semipermeable membrane of cupric ferrocyanide is formed in the shape of a drop by the addition of a small quantity of copper sulfate solution, which also contains albumen and sucrose or glucose in varying concentrations, to a solution of potassium ferrocyanide. Differences in osmotic pressure, or more precisely differences in tonicity, between the two solutions, are obtained by means of the various concentrations of the sugars. The diffusion of water into the drop is accompanied by the formation of potassium sulfate. When the concentration of this salt becomes sufficiently large turbidity is produced in the drop due to the coagulation of the albumen. The time necessary for the initial appearance of this turbidity is an indication of the rate of penetration of the water into the drop which in turn is an indication of the osmotic pressures of the solutions of sucrose and glucose. The procedure is a modification of the methods suggested by Chodat[1] for the qualitative demonstration of osmosis.

Egg white, or a saturated solution of albumen, is added to a saturated solution of copper sulfate. A 1:3 ratio of the albumen to the copper sulfate solution is recommended. From this solution are prepared solutions containing 1.25, 2.5, 5.0, and 10% (by weight) of sucrose and glucose. An 8% solution of potassium ferrocyanide is found to give excellent results.

The potassium ferrocyanide solution is placed in a shell vial to a depth of about 5 cm. The diameter of the vial should be about 2 cm. The membranes formed should have the shape shown in Figure 1. This shape is obtained by using a dropping tube with an opening about 0.6 cm in diameter. The drop of copper sulfate solution should be released from a distance slightly above the surface of the potassium ferrocyanide solution. A little practice will enable the experimenter to

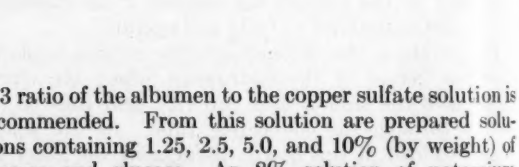


Figure 1.

[1] Thomas, P., "Manual de Biochemie," Masson, Paris, 1936, p. 100.

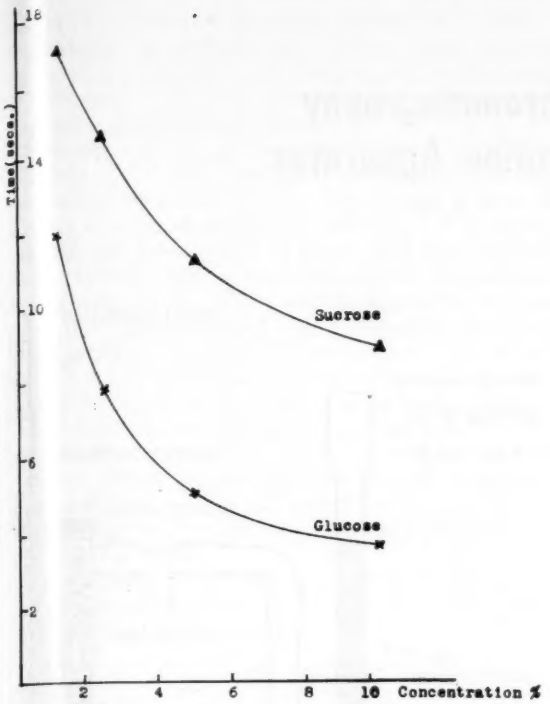


Figure 2.

produce uniformly satisfactory drops properly suspended from the surface of the solution in the vial.

The drop is then observed for the coagulation of the albumen. The time necessary for the first faint appearance of turbidity is noted with a stop watch. This first makes its appearance near the neck of the drop. At least three satisfactory determinations should be made with each concentration. The results of a series of determinations with the two sugars are plotted in Figure 2.

The drop should be observed against a black background. It should be illuminated with a bright beam from above and the drop should be observed at right angles to the beam. Changes in the size and shape of the drop should also be recorded. In general the enlargement of the drop due to the diffusion of the water manifests itself in a general lengthening of the drop. After the appearance of the turbidity the drop can be detached from the surface by means of a stirring rod. After it has dropped to the bottom of the vial, and any adhering portions cleared from the surface, a new drop can be formed in the same solution. In this manner a number of determinations can be made with the same portion of potassium ferrocyanide.

Egg white, or a saturated solution of albumen, give equally satisfactory results. However the egg white must be fresh or must have been stored in a cool place.

The rate of flow into the drop is affected very appreciably by changes in temperature. Hence a series of determinations must be carried out at essentially constant temperature. The effect of temperature is shown in Figure 3. The solution in this case contained 1.25% sucrose. Because of the temperature effect on the rate of flow it is not possible to use this experiment to study the direct effect of temperature change on the absolute magnitude of the osmotic pressure.

As stated in the opening paragraph the time necessary for the first appearance of turbidity, at constant temperature, is a measure of the rate of flow of the water into the drop and hence a measure of the relative tonicities of the solutions inside and outside the membrane. As seen in Figure 2, the time necessary for turbidity for a given weight per cent of the two sugars is roughly 2:1, essentially the ratio of the molecular weights, and hence the ratio of the osmotic effects produced by each.

The formation of the turbidity is apparently due to the increasing concentration of the potassium sulfate in the drop. This is formed as the potassium ferrocyanide reacts with the copper sulfate. The membrane of cupric ferrocyanide is apparently permeable to the various ions present. The over-all processes taking place and the changes in concentration are probably quite complicated.

The procedure described can be modified in a number of respects to produce a project-type experiment. The rate of flow with varying concentrations of various salts within and without the drop can be studied. Other solutes impermeable to the membrane could be added to the copper sulfate solution. Consideration can be given to the effect of changes in the concentrations of various added substances on the coagulation of the albumen.

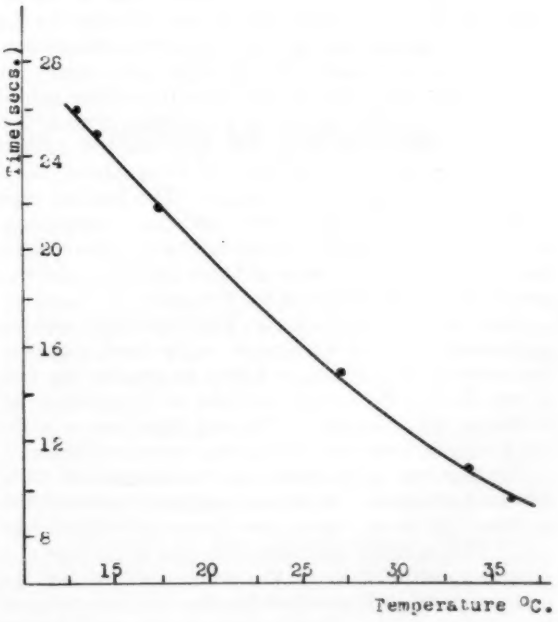


Figure 3.

Acknowledgment

The author is most grateful for the critical appraisal of this experiment by Mr. Thomas B. Douglas, a senior chemistry major working under the direction of Professor H. D. Crockford at the University of North Carolina, Chapel Hill.

Paul J. Cowan[1]
and **James M. Sugihara**
University of Utah
Salt Lake City

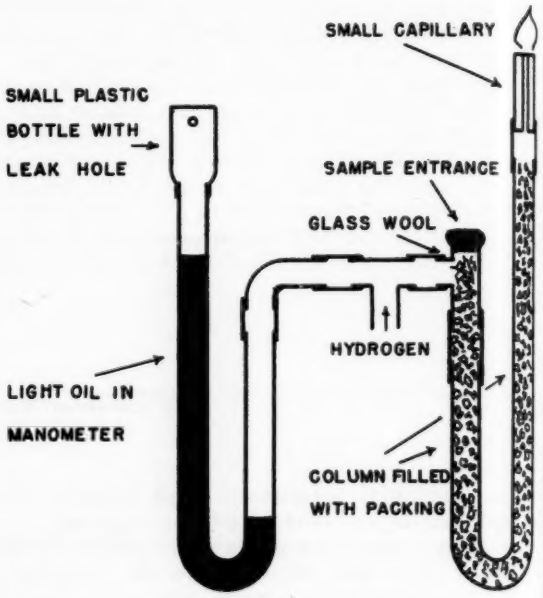
A Gas Chromatography Demonstration Apparatus

Chromatography is one of the most valuable methods available for the separation of mixtures. A lecture demonstration or a student experiment dealing with paper or column chromatography is readily accomplished. However, an extension to gas chromatography presents some difficulties. In the work described herein, an inexpensive apparatus was constructed and shown to effect satisfactory separations of mixtures of several organic liquids. Detection of the components in the effluent stream was accomplished using a simplified version of the method described by Scott,[2] who measured changes in temperatures above a hydrogen flame by means of a thermocouple. In this study a visual observation of changes in nature and height of the flame was found to permit a semiquantitative detection.

A four-foot length of 6-mm glass tubing was bent into a U-shape with one leg about twice as long as the other. A glass tee was attached to the short end, and the vertical opening was closed with a rubber serum bottle cap. A second tee was attached to the horizontal opening and the resulting two openings connected to a manometer and the hydrogen source. A wad of glass wool was placed below the rubber cap to provide increased solid surface to facilitate evaporation of the sample. A heating tape was wrapped around this section of the apparatus to bring about rapid evaporation of the liquid sample. The heating tape may be extended to the U-tube, permitting chromatography at higher temperatures for mixtures of less volatile compounds. A short piece of 1-mm capillary tube was connected to the long end of the U-tube.

The U-tube was packed with Tide[3] detergent powder, previously screened to remove −100 mesh particles. the smallest particles were found to impede the rate of gas flow to the extent that the solid tended to be dislodged from the tube. Dinonyl phthalate on a fire brick support[4] was also used as the stationary phase.

The flow rate of hydrogen was varied between 35 to 300 ml per minute. In most experiments a rate of flow of about 100 ml per minute was found to be advantageous. This variable influenced the rate of passage of a given compound through the column but, within the limits applied, did not affect the degree of separation of the mixtures used. After hydrogen had flushed air from the system, the gas emitted through the capillary was



ignited. The sample (0.01 to 0.02 ml) was introduced through the rubber cap using a hypodermic syringe. The time of arrival of each of the components could be readily determined by a change in the characteristics of the hydrogen flame. The nearly colorless flame became luminous in the presence of organic compounds. The presence of halogenated substances was readily detected by attaching a coil of copper wire to the exit nozzle. A bright blue-green colored flame was obtained as described by Beilstein's test.[5]

The apparatus was calibrated for several compounds, and changes in the flame characteristics were noted. The time of arrival, the time required for the flame to reach maximum height, the time of disappearance, and the maximum height of the flame were determined for each of a variety of organic liquids, for example, ethyl ether, acetone, carbon disulfide, chloroform, carbon tetrachloride, benzene, toluene, ethylbenzene, and the xylenes. Flame heights rose from about 0.5 mm to as much as 8 mm depending upon the nature of the compound and the sample size. The duration of the luminous flame varied from about 15 seconds for ethyl ether to a little more than a minute for the xylenes but was again dependent upon the sample size. The flame reached its maximum height after approxi-

Abstracted from the Master of Science Education Thesis of Paul J. Cowan, University of Utah, June, 1958.

[1] Member of the Academic Year Institute, University of Utah, 1957–58.

[2] Scott, R. P. W., *Nature*, **176**, 793 (1955).

[3] A product of Procter and Gamble Co., Cincinnati, Ohio.

[4] A product of Central Scientific Co., Chicago, Illinois.

[5] Shriner, R. L., Fuson, R. C., and Curtin, D. Y., "The Systematic Identification of Organic Compounds," 4th ed., John Wiley & Sons, Inc., New York, 1956, p. 60.

mately one-third of the total time duration, indicating a small degree of trailing. The plot of flame heights versus time gave curves from which areas under each of the humps were found to correspond to the sample size in a semiquantitative fashion.

Different mixtures of compounds were found to be separable. The calibration dates were used to identify each of the components. Data (see Table 1) from a mixture of ethyl ether, carbon disulfide, carbon tetrachloride, and benzene gave a graph with four discrete humps with the order of appearance of the components in the order given. The complete separation of this mixture was effected using Tide detergent as the fixed phase, maintained at 60°. A mixture of ethyl ether, acetone, 1,1-dichloroethane, carbon tetrachloride, and chloroform appeared in the order given from a column packed with dinonyl phthalate on a firebrick support at a temperature of 110° (see Table 2). Separation was complete. With dinonyl phthalate as the stationary phase again at a temperature of 110°, benzene, toluene, ethylbenzene, and *o*-xylene were separable but not *m*-xylene and *p*-xylene.

The examples given below are merely representative of the types of separation possible in this simple illustration of gas chromatography.

Table 1. A Separation Using Tide Detergent

Compound	Time of appearance (min) Start	Max.	End	Nature of flame
Ethyl ether	0.60	0.65	0.75	Bright yellow
Carbon disulfide	0.85	0.90	1.10	Light-blue to lavender
Benzene	1.65	1.78	1.96	Bright yellow and smoky
Carbon tetrachloride	2.00	2.15	2.45	Blue turning to yellow and smoky

Column length = 200 cm; temp = 60°C; flow rate = 111 ml/min; sample size = 0.01 ml.

Table 2. A Separation Using Dinonyl Phthalate

Compound	Time of appearance (min) Start	Max.	End	Nature of flame
Ethyl ether	0.94	1.00	1.12	Bright yellow
Acetone	1.28	1.40	1.62	Yellow
1,1-Dichloroethane	1.82	1.90	2.05	Light-blue turning to yellow
Carbon tetrachloride	2.46	2.60	3.04	Blue turning to yellow and smoky
Chloroform	3.55	3.70	4.30	Blue turning to yellow and smoky

Column length = 165 cm; temp = 110°C; flow rate = 88.5 ml/min; sample size = 0.02 ml.

Otto M. Smith,[1] **Otis C. Dermer,** and **Thomas E. Moore**
Oklahoma State University
Stillwater

Speeding the Training of Chemists

Until recently, there has been little effort on the part of college and university instructors and administrators to recognize that gifted and superior students can accomplish the usual college work in far less time than the average student, and to make satisfactory regulations and schedule arrangements so that these talented students may move as fast as their abilities and desires permit.

Speeding the training of the college student taking college general chemistry is more than just shortening the time required for the completion of this course. It is training the student to utilize the knowledge and skills gained in high school science courses and from personal reading, to acquire better study habits and use study time more effectively.

This article discribes a program for the freshmen who have above average ability and who have high school chemistry. It is based on 24 years of experience.[2]

At Oklahoma State University (A & M College), 2200 students have satisfactorily completed in one semester of four credit hours the same material in college general chemistry as is usually taught in the two-semester class.

This plan is based on the following principles:

(1) General chemistry is a course designed for any college-caliber student who wishes or needs the fundamental knowledge presented therein.

(2) The general chemistry course is a service course, and its function is to cover the accepted ground work for all students as rapidly as possible. The more rapid class of one semester covers essentially the same material, except the laboratory, as the two-semester class.

(3) One objective is to avoid the development of poor study habits by gifted students. These are challenged, stimulated, encouraged, and forced to exercise their mental abilities and capacities toward greater accomplishments. They have capacities which, in many cases, have never been fully challenged. So the plan is to make assignments of sufficient length and difficulty to make all the members of the class work and to keep them working at a high tempo throughout the semester.

(4) College students expect and should receive recognition and emoluments for a semester of good work. No practice has proved so essential toward the success of a class of superior and gifted students as the assurance of fair competition for grades.

Presented before the Division of Chemical Education at the 133rd Meeting of the American Chemical Society, San Francisco, April, 1958.

[1] Present address: Kansas State Teachers College, Emporia, Kansas.

[2] Smith, Otto M., J. Chem. Educ., **33**, 539 (1956).

It is through good grades that students are placed on the honor rolls and receive bids from honor societies, from fraternities or sororities. Scholarships are offered to them, and many other honors are bestowed upon the high-ranking students.

(5) Students in the one-semester class are not penalized for trying, should they be unable to make the desired progress. They are not failed, but, rather transferred at appropriate periods to a slower moving two-semester class.

(6) Four hours of college credit in general chemistry are given to those students who demonstrate by written and oral examinations that they have as good a knowledge and laboratory technique as the freshman students have at the close of the two-semester class.

Selection and Administration

Since 1928, all entering freshmen who are required to have a course in college general chemistry and who have had high school chemistry have taken the Iowa Training Test in Chemistry; some of the better prepared also take the ACS General College Chemistry Test. Forty to 50% of these high school students make a score of 80 or above in the Iowa Chemistry Training Tests and thus are sufficiently prepared for and are scheduled in the rapid, one-semester class.

Some, of course, object and want to take the easier and longer path. Nevertheless, they are urged to remain in the class until mid-term; then, if they still want to change, they may transfer to the two-semester class. In most cases, the better students respond and elect to remain. Those who do not make satisfactory progress are transferred to the two-semester class. Parallel schedules are provided to simplify the transfer.

Over the twenty-four years, this class has varied from 55 to 159 students per year, or from 5.8 to 17.6% of the entire freshman general chemistry class. This one-semester class is largely made up of engineers, premedics, and science majors.

The one-semester class is conducted like most classes, except that considerable emphasis is placed upon the necessity that the student utilize the knowledge and skills gained in high school. Of course, the assignments, are much longer than is customarily given to the two-semester class. After a little training and conditioning, the student finds that he can "take it" and usually does excellent work. Until recently, the same textbook and laboratory text manuals were used.

In conducting a class for the more talented students, no other factor is as important as that of assigning grades. Throughout the semester the students are assigned rank position while treating the one-semester class as a unit, but when the final grades are given, the grades are assigned as if this select one-semester class were a part of the entire group of freshmen taking general chemistry. To obtain a basis of comparison between the performance of the one-semester group and the two-semester group, a form of the ACS General College Chemistry Test is administered as part of the final examination. This same or a similar test had been given to the previous year two-semester class of students, thus it is possible to obtain a relationship between the grades to be awarded and the percentile score made on the ACS test. In this way, the professor can estimate with fair accuracy the probable grade the student would have made if he had been a member of the two-semester group.

In most cases at the end of the semester the student is given higher grades than he expected to receive, and, naturally, he is very pleased. Since the students of this class are a select group, they should be expected to receive a large number of high grades. For example, during the past nine years, the A and B grades varied from 46% to 66% of grades assigned each year in the one-semester class.

Results

In looking back over the twenty-four years, the chemistry faculty of the university are convinced that these 2200 students have done as well in their work in other subjects and subsequent chemistry classes as the regular students. There is considerable evidence that they have done even better.

How has the university profited? About one-third of a professor's time during one semester may be used for other work. More than the value of the time gained is the good will of the more energetic, talented, and capable students. By using this plan, the university has enabled these 2200 students to each have four credit hours of additional work, an over-all total of 8800 credit hours. This is equivalent to the work which 73 students would complete in four years, and has a high monetary value.

The student has benefited by completing in four-semester hours a course that usually requires eight hours, thus gaining four hours to use for an additional course of his choice or in his major field of study. He has learned to study effectively and to use what he has learned in high school and elsewhere. He is challenged to do his best work in order to keep up with the other students of exceptional ability. He can make a grade as high as that which he would make when placed in competition with the lesser prepared students. He encounters no risk of receiving a low or failing grade and his chances for receiving honors or election to honor societies are not impaired. He has everything to gain and nothing to lose.

Molality-Molarity Paradox—A Second Look

(*Continued from page 230*)

The situation arises by imposing too many restraints on the system. If we write the relationship between m and M in the form

$$\frac{M}{m} = \frac{Wd}{W + w}$$

it is clearly impossible for m to equal M and simultaneously for d to be less than unity.

SIDNEY TOBY
Rutgers University
New Brunswick, N.J.

Stephen R. Cohen
Brown University
Providence, R. I.

The Use of Energetics in Elementary Biochemistry and Physiology

Energetics is frequently neglected in a first course in biochemistry or physiology, or in the usual general course in these subjects taken by premedical students or by student nurses. These courses are often descriptive. The mechanism of important processes is presented in considerable detail, while the consideration of energetics if often limited to the "calorie values" of foods and some qualitative discussion of the high-energy phosphate bond. This is unfortunate because energetics can provide the student with insights into over-all physiology which are independent of the mechanisms involved, and which are not otherwise apparent. In addition, the simplicity and elegance of the subject, its ability to demonstrate general truths with a minimum of difficult formal manipulation, are often appealing to the good students.

The quantitative treatment of energetics may be omitted because the topic is felt to be too difficult and to require some prior knowledge of physical chemisty. Actually, the study of energetics is frequently easier than the study of mechanisms with its emphasis on detail and memorization. Often it only requires arithmetic, some very elementary physics, and close attention to the actual physical situation. To illustrate, I shall briefly present several elementary applications of energetics to these subjects.

Living organisms are, among other things, heat engines, and can be studied as such. In so doing, it is important to know the energies available from foodstuffs when used as "fuels." The catabolism of fatty acids is by "β-ketonic" oxidation. By a complicated series of reactions, a two-carbon fragment of the alkyl chain together with its four associated hydrogen atoms is split off and oxidized to carbon dioxide and liquid water. Stearic acid, $CH_3(CH_2)_{16}COOH$, is degraded to palmitic acid, $CH_3(CH_2)_{14}COOH$, which in turn becomes myristic acid, $CH_3(CH_2)_{12}COOH$, then lauric acid, $CH_3(CH_2)_{10}COOH$, and ultimately butyric acid, $CH_3(CH_2)_2COOH$, or acetic acid, CH_3COOH.

$$CH_3(CH_2)_{14}CH_2CH_2COOH \rightarrow CH_3(CH_2)_{14}COOH + (—CH_2CH_2—) \quad (1a)$$

(Stearic acid) (Palmitic acid) (2-carbon fragment)

and

$$(—CH_2CH_2—) + 3O_2 \rightarrow 2CO_2 + 2H_2O \quad (1b)$$

or over-all,

$$CH_3(CH_2)_{16}COOH + 3O_2 \rightarrow CH_3(CH_2)_{14}COOH + 2CO_2 + 2H_2O \quad (1)$$

The energy made available by this process and the dependence of this energy on the chain length can be found from elementary thermochemistry. The heat of a reaction depends only on the reactants and products and not on the details of the process. Therefore the heat of combustion of stearic acid burning directly to carbon dioxide and water (equation 2) is equal to Q, the heat released by splitting off and burning a two-carbon fragment (equation 3), plus the heat of combustion of the resulting palmitic acid (equation 4).

$$CH_3(CH_2)_{16}COOH + 26O_2 \rightarrow 18CO_2 + 18H_2O + 2711.8 \text{ kcal}^1 \quad (2)$$

$$CH_3(CH_2)_{16}COOH + 3O_2 \rightarrow CH_3(CH_2)_{14}COOH + 2CO_2 + 2H_2O + Q \quad (3)$$

$$CH_3(CH_2)_{14}COOH + 23O_2 \rightarrow 16CO_2 + 16H_2O + 2398.4 \text{ kcal} \quad (4)$$

Algebraically

$$2711.8 \text{ kcal} = Q + 2398.4 \text{ kcal}, \text{ and } Q = (2711.8 - 2398.4) \text{ kcal} = 313.4 \text{ kcal}$$

Obviously the heat released by the "β-ketonic" oxidation of any fatty acid may be similarly computed.

Subtracting the heats of combustion of successive even-carbon fatty acids shows that about 314 kcal per two-carbon fragment (or 157 kcal per carbon atom) are liberated by "β-ketonic" oxidation, regardless of chain length.[2] Although the process occurs at the carboxylic end of the molecule, the reactants and products, and consequently the heat released do not depend on the location of the carbon atoms along the alkyl chain. The same value would be found even if the two carbon atoms were separated. One half the heat of "β-ketonic" oxidation, 157 kcal (11.2 kcal per gram) is the heat of combustion of *any* carbon atom with its two hydrogen atoms, (—CH_2—), from *any* typical alkyl chain. (It is interesting that the 157 kcal liberated by removing and burning a (—CH_2—) fragment from an alkyl chain is remarkably close to the 164 kcal liberated by burning the same amount of carbon and hydrogen separately.) Therefore it is also the catabolic value per carbon atom of the alkyl chain of an amino acid. If the contribution of the terminal carbon atoms is ignored, or estimated separately, it is also an estimate of the heat of combustion per carbon atom, or per gram, of a commercial hydrocarbon fuel. These conclusions can be verified by subtracting the heats of combustion of successive homologous amino acids, or successive straight-chain paraffin hydrocarbons. The accepted calorie value of about 9 kcal per gram for a typical fat

[1] Thermochemical data are available in standard handbooks of chemistry, texts on thermochemistry or thermodynamics, and United States Bureau of Standards Circular 500.

[2] Heats of reaction rather than free energies are used throughout because they are more accessible, and their use does not seriously affect the results. They are actually preferable when heat production is a major function of a process.

is an average of 11.2 kcal per gram for the "β-ketonic" degradation of the fatty acid chains, 3.5 kcal per gram for the oxidation of the acetic acid produced by this process, and 4.3 kcal per gram for the glycerol.

The gross catabolism of carbohydrates may be treated similarly. The heats of combustion of representative hexoses and polysaccharides to carbon dioxide and liquid water (equations 5, 6, 8*b*, 9*b*) range from about 112 to 113 kcal per carbon atom (673 to 679 kcal per six-carbon unit), indicating that the heats of isomerism and of hydrolysis of the polysaccharides are negligible.

$$\underset{\text{(fructose)}}{C_6H_{12}O_6} + 6O_2 \rightarrow 6CO_2 + 6H_2O + 675.6 \text{ kcal} \quad (5)$$

$$\underset{\text{(starch)}}{(C_6H_{10}O_5)_x} + 6xO_2 \rightarrow 6xCO_2 + 5xH_2O + 677.6\ x \text{ kcal} \quad (6)$$

$$\underset{\text{(graphite)}}{C} + O_2 \rightarrow CO_2 + 94.4 \text{ kcal} \quad (7)$$

(Depending on extent of condensation with loss of water these values range from 3.73 kcal per gram for glucose to 4.19 kcal per gram for glycogen.) The heat of combustion of graphite is 94.4 kcal per gram atom of carbon (7.86 kcal per gram) (equation 7). In using carbohydrates an organism can be considered to be burning carbon with the hydrogen and oxygen contributing little energy. The carbon may be considered to be combined in carbohydrates to enable it to be transported easily and to permit low-temperature controlled oxidation. This convenience must be paid for; combined, carbon provides 4 kcal per gram of carbohydrate, rather than the 8 kcal per gram for graphite.

Analogous anaerobic and aerobic processes for the utilization of a substance are quite common. Sometimes these processes are found in different species; sometimes the same species uses both processes. The fermentation of glucose to ethyl alcohol (equation 8*a*) and the conversion of glycogen to lactic acid in the muscles (equation 9*a*) are typical anaerobic processes; the complete oxidations of glucose (equation 8*b*) or of glycogen (equation 9*b*) are the aerobic analogues.

Anaerobic:

$$\underset{\text{(glucose)}}{C_6H_{12}O_6} \rightarrow \underset{\text{(ethyl alcohol)}}{2C_2H_5OH} + 2CO_2 + 18 \text{ kcal}^3 \quad (8a)$$

$$\underset{\text{(glycogen monomer)}}{(C_6H_{10}O_5)} + H_2O \rightarrow \underset{\text{(lactic acid)}}{2CH_3CH(OH)COOH} + 21 \text{ kcal} \quad (9a)$$

Aerobic:

$$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O + 673 \text{ kcal} \quad (8b)$$

$$(C_6H_{10}O_5) + 6O_2 \rightarrow 6CO_2 + 5H_2O + 678.8 \text{ kcal} \quad (9b)$$

The heats of alcoholic fermentation and of lactic acid formation are 18 kcal per mole of glucose, and 21 to 45 kcal per mole of glycogen monomer (depending on whether the product is considered to be lactic acid, as in the equation, or lactate ion). Contrasted to the heat of combustion of 763 kcal per mole of glucose and 679 kcal per monomer of glycogen, these are very "inefficient" processes, releasing 2.6 to 6% of the available energy. However, they have the great advantage of not requiring an external supply of oxygen. Thus fermentation is an alternate mechanism used by yeast under anaerobic conditions. Similarly lactic acid production from a stored reserve of glycogen enables muscles to react suddenly, in emergencies, without requiring an immediate increase in oxygen supply from the blood. The production of lactic acid (or pyruvic acid) in muscles is associated with an aerobic process which converts most of the lactic acid to carbohydrate, the energy for this process being provided by the complete oxidation of a small amount of lactic acid (or pyruvic acid). From the "efficiency" given above for the first process, roughly 94 to 97% of the lactic acid can be converted to glycogen in this second process. Actually the process is not this efficient; only about 80% is reconverted.

Frequently "energy balances" can provide information about processes which cannot easily be studied experimentally. The internal organs are primarily cooled by the circulation; the removal of heat from the liver is a good illustration. Assume a typical man produces 1.67 kcal of heat per minute (2400 kcal per day) of which 30% or 500 cal per minute is produced by the liver.[4] The circulation of the blood averages 5000 ml per minute of which 10 to 20% or 500 to 1000 ml passes through the liver. If the heat capacity of blood is approximately 1 cal/ml°C, then the blood in passing through the liver is heated 0.5° to 1°C (depending on whether the higher or the lower estimate for the circulation is chosen). Symbolically:

$$t = \frac{Q}{W \times C} = \frac{500 \text{ cal/min}}{500 \text{ ml/min} \times 1 \text{ cal/ml°C}} = 1°C$$

where t = temperature rise, Q = quantity of heat produced, W = quantity of substance absorbing heat, and C = heat capacity of substance absorbing heat. Even if half the heat were removed by conduction to surrounding tissues (which is unlikely), the temperature rise would still be 0.3° to 0.5°C. Thus, by this analysis, a reasonable estimate was made without experimentation. Because of the local inflammation produced by thermometers of thermocouples inserted into internal organs, direct measurements might be less reliable.

There are obviously many other applications of energetics which provide similar general insights with the same minimum of physics and mathematics. It is surprising, therefore, that this approach, with its simplicity, power, and elegance, is so often neglected in courses, and even in research, in biochemistry and physiology. This is ironic when it is recalled that the concept of the conservation of energy was first proposed in 1845 by J. R. Mayer, a physiologist.

[3] The values are for pure reactants and products. Because of the heats of solution, the values will be slightly different for the same reactions within a living cell.

[4] These values are taken from standard physiology texts. Because only a rough estimate is being made, specific sources are not given.

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Frederick T. Wallenberger,
William F. O'Connor,
and **Emil J. Moriconi**
Fordham University, New York, N. Y.

A Simple Universal Apparatus for Steam Distillation

As a standard laboratory operation, the time-consuming art of steam distillation using conventional apparatus suffers from certain inherent disadvantages: in indirect steam distillation where the steam is generated in a separate flask or obtained from a steam line, it involves generation and handling of live steam; in direct steam distillation where the steam is generated *in situ* in the distilling flask, only limited amounts of water and organic substance can be distilled. Further, in both direct and indirect steam distillation the equipment is unwiedly and its manipulation difficult, especially when the steam is generated at the bench; large volumes of water are distilled to recover small amounts of organic substance. If the organic product (e.g., quinoline, citral) is partially water soluble, the large volume of water condensate must be further concentrated, or extracted, to recover organic product; and solids may crystallize in the condenser with consequent interruption of the distillation process.

To circumvent some of these difficulties, several varieties of steam distillation apparatus for specific preparations have been described with (*1a*), and without (*1b*, *2*, *3*, *4a*) provision for return of water condensate to the distillation flask. Further, there are available several types of automatic separators (*4b*, *4c*, *4d*, *4e*, *5a*, *5b*, *6*, *7*) which may be adapted for steam distillation purposes. Nonetheless, it has been the authors' experience that, at the undergraduate preparatory level and in academic and industrial research, the conventional apparatus described in organic laboratory manuals (*8*, *9*, *11*, *12*, *13*) is most often resorted to.

On a recent visit to the Jackson Laboratory, Research Division, Organic Chemicals Department of E. I. du Pont de Nemours and Company in Wilmington, Delaware, one of the authors (F. T. W.) was shown a steam distillation apparatus[1] of simple design which could be used for substances both heavier and lighter than water. Further, it seemed to have none of the disadvantages of the conventional assembly.

This paper reports on an evaluation of a modification[2] of this apparatus hereinafter designated as a Universal Steam Distillation Apparatus, Figure 1, in comparison with a conventional steam distillation assembly and two special steam distillation assemblies of more elaborate design (*1b*, *2*).

In addition, we have also simplified the design of the apparatus (Fig. 2) so that its cost is no more than that of some of the standard equipment found in undergraduate organic lockers. This modified apparatus has no standard taper joints and the three-way stopcock has been replaced by a Y tube connected to the column and the receiver with Tygon tubing. Flow is controlled by three pinchcocks.

The all-glass apparatus (Fig. 1) is designed to accomplish steam distillations of all water-immiscible and steam-volatile organic liquids and solids, both heavier and lighter than water. Its operation is based on two principles: direct steam distillation and recycle of the condensed water phase. In brief, the heterogeneous mixture of water and organic substance is heated in the distilling flask to form the two-phase vapor. The condensate from the attached reflux condenser separates in the straight column which acts as a receiver when the three-way stopcock is closed. When water appears as the top layer, it continually overflows through the upper feedback into the distillation flask for reuse while the organic product accumulates in the receiver. When water appears as the bottom layer, its recycle is effected through the lower feedback via the three-way stopcock. In either case, the organic layer may be drawn off through the same stopcock at any time.

The apparatus has been used with round-bottom distilling flasks of 250–1000 ml capacity to recover approximately 30 ml of organic material. Since the organic layer can be continuously drained without disrupting the distillation process, the receiver capacity is unlimited.

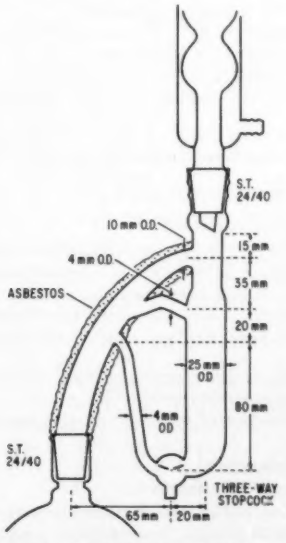

Figure 1. Universal steam distillation apparatus.

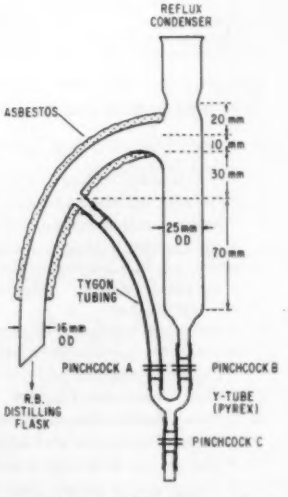

Figure 2. Modified universal steam distillation apparatus.

[1] Private communication: Dr. V. Weinmayr. The apparatus was designed by Adrian L. Linch, Chamber Works. It is made by the Ace Glass Co., Vineland, New Jersey, from drawing No. AI-33 designated as "Universal Water Separator," 125 ml size.

[2] The receiver jacket has been eliminated from the original design. Our apparatus was made by Eck and Krebs, Inc., Long Island City 1, New York.

Table 1. Comparison of Rate of Recovery of Organic Products in Steam Distillations Using the Universal Steam Distillation Apparatus and the Conventional Steam Distillation Assembly

Compound	Specific gravity[a,b]	Mp, °C[a]	Bp, °C[a,c]	Recovery of organic compound (g/min)		Reference
				The apparatus	Conventional assembly	
Benzene	0.879	5.5	80.1	13.2	15.0	(*8*) pp. 44, 118; (*9*) p. 57
Toluene	0.866	−95	110.6	5.8	4.7	(*9*) p. 58
p-Cymene	0.857	−68.0	177.1	3.4	2.8	.....
Mesitylene	0.867	−44.7	164.7	3.4	2.5	(*10*)
p-Diethylbenzene	0.862	−43.2	183.8	1.9	1.4	.....
Cyclohexene	0.810	−103.7	83.3	5.4	1.1	(*8*) p. 69
N,N-Dimethylaniline	0.956	2.5	194.2	2.4	1.0	(*11*) p. 433
Citral	0.890 $\frac{17°}{4°}$	...	228–229°	0.7	0.5[i]	(*9*) p. 59
n-Decanol	0.830	7	232.9	0.4	0.3	.....
Bromobenzene	1.495	−30.6	156.2	10.0	7.5	(*8*) pp. 43, 121; (*9*) p. 79; (*11*) p. 406
Iodobenzene	1.824 $\frac{25°}{4°}$	−31.3	188.5	6.2	2.8	(*9*) p. 60; (*12a*) p. 283; (*12b*) p. 246
Nitrobenzene	1.203	5.7	210.9	3.3	1.4	(*9*) p. 256
Aniline	1.022	−6.1	184.4	2.2	1.8[i,j]	(*9*) p. 149; (*13*) p. 234; (*11*) pp. 365, 386, 470
o-Dichlorobenzene	1.306	−17.2	180.4	2.9	1.9	.....
m-Bromotoluene	1.410	−39.8	183.7	2.5	2.5	(*14*)
Acetophenone	1.028	19.6	202.0	2.0	1.3	(*12a*) p. 339; (*12b*) p. 292
s-Tetrachloroethane	1.600	−36	146.2	8.0	5.8[i]	(*15*)
Pentamethylbenzene	0.847 $\frac{107°}{4°}$	54.3	230–231	0.70[g]	0.08[k]	.....
Biphenyl	0.992 $\frac{73°}{4°}$	70.5	256.1	0.20[g]	0.06[l]	(*13*)
Naphthalene	1.145	80.2	218.0	1.20	0.80	(*8*) p. 44
p-Dibromobenzene	2.261 18°	87.3	220.3	0.18[h]	0.03	(*8*) p. 121
o-Iodonitrobenzene	1.883 $\frac{100°}{4°}$	52–54	288–289/729 mm	0.20[k]	0.10	.....
o-Nitrophenol	1.295 45°	45.0	217.2	0.66[k]	0.09[i]	(*12a*) p. 246; (*12b*) p. 214; (*13*) p. 279
o-Phenanthroline	...	117.0	300	0.62[k]	0.10	.....
Diphenylamine	1.160 $\frac{20°}{20°}$	52.9	302	0.09[k]	0.06	(*16*)
Benzophenone	(α) 1.083 54°	(α) 48.1	305.9	0.12[k]	0.06[k]	.....
Azobenzene	1.203	68	297	0.22[k]	0.06[k]	(*17*)
Quinoline (Skraup)[d]	1.095 20°	−15.6	237.1/747 mm	0.4	0.2	(*1b*)[o]
β-(3-Acenaphthoyl)-propionic acid (Friedel-Crafts)[e]	...	206–208	...	3.3	1.4	(*2*)[m]; (*9*) p. 256
1-hydroxy-1-phenyl-1,2,3,4-tetra hydronaphthalene (Grignard)[f]	...	135–140	135–140/2 mm	0.3	0.1[n]	(*18*)

[a] Physical data from N. A. Lange "Handbook of Chemistry," 8th ed., Handbook Publishers, Inc., 1952, unless otherwise noted.

[b] Specific gravity data $\frac{20°}{4°}$ unless otherwise noted.

[c] Bp data at 760 mm unless otherwise noted.

[d] Solvent nitrobenzene and the reaction product quinoline are successively steam distilled from the reaction mixture.

[e] Solvent nitrobenzene is steam distilled from the reaction product β-(3-acenaphthoyl)-propionic acid.

[f] Steam distillation removes unused bromobenzene and α-tetralone, and Grignard by-products: benzene, biphenyl, etc. from the reaction product 1-hydroxy-1-phenyl-1,2,3,4-tetrahydronaphthalene.

[g] Receiver solvent: toluene; other suggested receiver solvents lighter than water: petroleum ether, methylcyclohexane, cyclohexane and *n*-butyl ether.

[h] Receiver solvent: chloroform; other suggested receiver solvents heavier than water: chlorobenzene, 1,2-dichloroethane, carbon tetrachloride, 1,2-dibromoethane and dibromomethane.

[i] Partially water-soluble; extraction of water condensate necessary for complete recovery of organic product.

[j] Slow separation of layers.

[k] Slow solidification of organic product.

[l] Steam distillation with super heated steam.

[m] The special assembly described in this reference has a recovery rate of 5.7 g/min.

[n] Requires a tedious steam distillation on a heat sensitive product.

[o] The special assembly described in this reference with a recovery rate of 0.4 g/min includes two large condensers, 12-liter distilling flask and receiver; over 12 liters of distillate are collected.

Operating Procedure

For convenience, the distilling flask should be about one-half filled. However, not less than 200 ml of water should be used. The use of boiling stones is recommended. Heating may be supplied by either a heating mantle or burner.

Organic liquids are steam distilled and collected by a proper setting of the three-way stopcock. For liquids of density slightly higher than water, the condensed heterogeneous phase sometimes does not properly separate, and forms an immiscible additional top layer. This appears to be a surface phenomenon which may be eliminated by simply extending a thermometer through the condenser into the apparatus so that its lower tip rests 1 to 3 mm above the liquid level. The droplets of condensate originating on the thermometer will sufficiently break the surface film to facilitate the separation of layers.

Organic solids are distilled in the same manner, but are collected in a proper water-immiscible organic solvent. The solvent is placed into the receiver before distillation to fill approximately two-thirds of its capacity. A solvent should be selected so as to make the final solution of solid in the solvent considerably lighter or heavier than water. In this manner a possible interchange of layers during the distillation is avoided. The solvent should have a boiling point greater than 80°C, since this is the approximate temperature in the receiver during distillations. Suggested receiver solvents are found in Table 1. If this solvent, containing distilled solid, is withdrawn from the apparatus during distillation, it may be replaced through the condenser. To recover the desired organic product, the collecting solvent may easily be removed via steam bath or water aspirator.

Efficiency of Operation

As an approximate measure of the relative efficiency of the apparatus compared to conventional steam distillation assembly, rates of recovery of organic material have been studied for some 30 compounds. For organic liquids, 10–30 ml of material was steam distilled and the volume of condensed immiscible organic material measured. Organic solids (1–10 g) distilled in the conventional assembly were filtered, dried and weighed. When distilled using the apparatus, the receiver solvent was drained, evaporated to dryness, and the residue weighed. In all cases, the rate of recovery is reported in grams of organic material recovered per minute for time intervals less than that required for quantitative recovery.

The results summarized in Table 1 indicate that with the exception of benzene and *m*-bromotoluene, recovery rates with the apparatus are considerably faster than those using the conventional assembly. The higher recovery rates for the apparatus may be due to the generation of slightly superheated steam in the vigorously heated flask and to the efficient transport of the heterogeneous vapor from the distilling flask to the condenser.

More elaborate assemblies are available for the preparation and steam distillation of quinoline (*1b*) and for the steam distillation of solvent nitrobenzene from β-(3-acenaphthoyl)propionic acid (*2*). In this evaluation it was found that the recovery rates with these special assemblies are much better than with the conventional assembly and are comparable to or somewhat better than with the apparatus.

Although these high recovery rates are extremely desirable in the art, it should be noted that the most outstanding feature of the apparatus is its unique recovery procedure.

Acknowledgments

We are indebted to Dr. Victor Weinmayr for his interest and cooperation in this evaluation. The assistance of Fordham graduate and senior students is greatly appreciated: John L. Ferrari and James F. Riordan made the apparatus described in Figure 2; John Barone, Robert Keane, and Matthew Moran ran some of the steam distillations.

This work was supported in part by a grant from the Research Corporation, and in part by a grant (C-3325) from the U.S. Public Health Service, National Cancer Institute. Grateful acknowledgment is hereby made.

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Personalities and Trends

The new chancellor of the University of California at Berkeley is Glenn Seaborg, whose name is synonymous with an abrupt change in outlook which has come to so many areas of our recent technological society at the international level. It is only fitting that he be placed in the capacity of chancellor of the "Queen University of the West." His influence will be felt in perpetuating the dignity of integrity for which the University of California has long been known and which is needed in all areas of education in our state, where radical changes must take place in the near future. An unprecedented expansion of campuses within the state college system and also within the university system is being planned. The growing pains are terrific and many glaring mistakes have been made, but by constantly open criticism, unharrassed by certain undemocratic principles that sometimes gain control, adjustments will be made. Nobel Prize Winner Seaborg has had, and will have, much to say about the future. For this reason, chemists are certain that an appropriate influence will be established in keeping pace with the times in which we live.

Norris Rakestraw of the Scripps Institution of Oceanography will participate in the International Oceanographic Congress to be held in New York in August. The University of California is establishing a full-fledged campus at La Jolla, in conjunction with the Scripps Institution. A physical chemist, James R. Arnold, has been added to the staff to develop the new chemistry department. San Fernando Valley State College is now under way and this next fall Alameda State College and Santa Anna State College will be added to the list of state colleges.

San Diego State College continues to lead the state colleges in research. A grant of $121,000 has been awarded to Arne Wick from the U. S. Public Health Service for the study of carbohydrate metabolism during the next five years. Lionel Joseph has received $6500 from the San Diego County Heart Association for the preparation of some benzimidazole derivatives as possible vasodilatory agents. Convair Scientific Laboratory has granted $10,000 to Drs. Landis and Wadsworth to continue work on the solution chemistry of titanium. Purchase of instrumental equipment for the chemistry department had been permitted through a grant of $18,000 from the Atomic Energy Commission. The new five-story, $3,500,000 chemistry building is scheduled for completion in December of this year. Robert Isensee is the new chairman of the chemistry department.

During his sabbatical leave from Stanford University last year, Arthur Furst presented papers at the International Cancer Congress in London and the International Psychopharmacology Congress in Rome. He also gave lectures or seminar talks while visiting laboratories in Scotland, Paris, Brussels, Tübingen, Basel, and Milan. He spent some time at the Sorbonne in Paris doing research.

The death of Hal Draper of Sacramento State College means a loss of a leader in the PSACT whose influence as a dedicated and versatile teacher has been felt in both the Fresno and Sacramento areas. A research fund has been established by the college in his name. Fred Nussenbaum has been appointed as head of the chemistry department to replace him. A three year grant-in-aid from NSF has been received by C. Robert Hurley to set up a research program in which both undergraduates and Master's degree candidates can participate.

At the University of San Francisco, the chemistry department has completed plans for its portion of the new science building that will soon be built. Mel Gorman spent last summer at the University of California on a NSF faculty fellowship. Dr. C. E. McCasland has received a NSF grant for research on the stereochemistry of alicyclic compounds. The National Institute of Allergy and Infectious Diseases of the U. S. Public Health Service made a grant to Robert Seiwald for continued work on the synthesis of fluorescent biological tracers.

Courtney Benedict of Chico State College attended an AAAS meeting in Washington, D. C. Chico State College has a NSF-sponsored Summer Institute planned for high school teachers of science and mathematics from June 15 through July 24, 1959. Norman Lofgren has had much to do in developing this program. Floyd Reese will give a refresher course in general chemistry with selected topics describing recent developments and trends in chemistry.

At the University of Southern California, Jerry Donahue has been an associate editor of the international volume on "Interatomic Distances," published by the Chemical Society of London. He has also been appointed a member of the U. S. National Committee of the International Union of Crystallography. David A. Dows was instrumental in bringing the Western Spectroscopy Conference to USC in February. A number of research workers from England and India are collaborating with K. J. Mysels on various projects related to micellular solutions. A program of research participation by high school and junior college teachers, suggested by Norman Karasch, has now developed into a nation-wide program under the auspices of the NSF.

Morris Hein of Mount San Antonio College has been appointed a member of the scientific committee to the air pollution control district of Los Angeles County. Ground has been broken for a new physical science center that will include five chemistry laboratories for the six full-time chemistry teachers on the staff.

J. A. Campbell, chairman of the chemistry department at Harvey Mudd College, has been appointed a member of the ACS Committee on Educational Films. He is currently undertaking a survey of all such films on chemistry subjects which now exist or are planned for production. Comments from all persons interested will be welcomed by him.

Robert H. Maybury of the University of Redlands is developing an intensive program of research dealing with proteins. He has purchased equipment, including an electrophoresis apparatus, an ultracentrifuge and a polarimeter with special features of his own design for high precision work. Support for his work has come from several sources, including the California Heart Association and the National Institutes of Health, with very substantial grants. The new chemistry building provides ample space for the intricate research being carried out. Redlands is celebrating its 50th anniversary and boasts of a graduate who became a recent president of the ACS, Roger Williams.

Word has been received by Rae Schwenck and Raymond Martin of Sacramento Junior College of the selection by the American Institute of Graphic Arts of their recently published laboratory manual "Basic Principles of Experimental Chemistry" as one of the 50 best books of the year. This manual accompanies the authors' textbook, "Basic Principles of Chemistry."

San Jose State College has been awarded three different summer institutes in the field of science and mathematics by the NSF. One of these, under the direction of Edward Harrington of the Science Education Department, has as its purpose to increase the competence of teaching science at the elementary school level. Another, under the supervision of Robert Patterson, will correct deficiencies of teachers adequately trained in only one of the two general subject areas of physical science or biological science. Recently added to the chemistry staff are Norman Albert in physical chemistry, Ralph Fessenden in organic chemistry, Oliver Lien in biochemistry, and Abraham Ottenberg in physical chemistry.

Immaculate Heart College has been offering a course and series of lectures sponsored by the NSF for chemistry teachers, headed by Sister Agnes Ann Green, president of PSACT. Lecturers included Anton Burg of USC, Aarie Haagen-Smit of Caltech, J. A. Campbell of Harvey Mudd College, and K. J. Mysels of USC. Dr. Leo Geller of the University of Tübingen is teaching laboratory project work at Immaculate Heart College this year.

Sister Gilmary is at Fordham University, on leave of absence while pursuing a Ph.D.

One of the "students" at Immaculate Heart College has been Dorothy Craig of Marlborough School for Girls. Also, she has been alumnae president of Iota Sigma Pi, honorary women's chemistry society.

Fresno State College added Dale Burtner to its staff in analytical chemistry. He comes from Shell Development Company and received his B.A. and Ph.D. from Reed College and the University of Washington, respectively. Bill Miller is working with Ennis Womack, chairman of the department, on a text of physical science. Ray Bremner has plans for a sabbatical leave next year in Pakistan, financed in part by a Fulbright Fellowship. Ennis Womack will attend the Boston Meeting of the ACS in behalf of the chemistry department and its accreditation. Warren Biggerstaff is excited over a grant, to be announced later, for some of his research that has kept several students busy, including Kenneth Stevens. Last summer, Warren Kilday held a three-month summer, undergraduate, research fellowship sponsored by the California Heart Association. This year James Seay and Leon Yengoyan held undergraduate scholarships made possible by the Fresno County Heart Association. These Heart Associations have sponsored work directed by Jack Abernethy on various phases of enzyme-catalyzed reactions. During this summer, June 22 to July 31, 1959, the NSF will sponsor a Summer Institute at Fresno State College.

Meetings

The Southern Section of the PSACT met at the University of Southern California on October 8, 1958. The program included Dr. Edward Fuller of Beloit College, who gave a lively talk on "What Every Young Chemist Should Know," Richard Miller of Los Angeles High School, who spoke on "High School Chemistry as It Is and as It Should Be," Richard Burt of Manual Arts High School, who presented the topic "The Summer 1958 Advanced Chemistry Laboratory Class Held at Los Angeles High," Jack Strauss of Hamilton High School, who talked on "Instruction on Radioisotopes as Carried Out in the Los Angeles City High Schools" and Dr. Edward Partridge of USC who presented "The Program of the TLARGI Rubber Technology Program."

On November 22, 1958, Gerald Thomas of San Francisco State College served as host to the Northern Section of the PSACT in their new chemistry building. Gerald Ballou introduced the speakers. Bert Morris described the course given at San Jose State College in Instrumental Analysis. The philosophy of the course was based on emphasis of the theory and use of instruments. Carl Noller of Stanford University presented his views on teaching organic chemistry to majors and non-majors in chemistry. If possible these students should be separated in order better to meet the needs of each group. He felt that descriptive material and practical applications were very worth while and that a study of structure, nomenclature, bonds, properties, and reactions was essential. A study of baccalaureate degrees offered in chemistry by 64 colleges in the U. S. was reported by S. W. Morse, based on his findings on a tour of the nation. Many differences were observed in requirements of language units and general education, as well as the title of the degree, whether B.A. or B.S. A discussion of the graduate program in the state colleges of California was presented by Warren Biggerstaff of Fresno State College. Most programs require research, foreign language, and a thesis. Problems of the present and future were brought out. Charles M. Shaw, research chemist and product engineer for Standard Oil Company and chairman of the Education and Manpower Committee of the California Section of ACS ended the program with a talk on "A Chemist Looks at Science Teaching and Teaching Scientists." Problems related to students, teachers, and parents were mentioned.

The state PSACT meeting was held at San Luis Obispo on the Cal Poly campus on January 2 and 3, 1959. Glenn Wight planned an excellent program and served as host for the meeting. A talk on "Air Pollution, Nature of Pollutants, Analytical Determination and Health Implications" was given by Meyer D. Thomas of the Stanford Research Institute. Fredrick L. Schaffer of the Virus Laboratory at UC spoke on "Poliomyelitis Virus, Current Knowledge of Its Physico-Chemical Nature." Then James N. Schoolery of Varian Associates presented the subject "Nuclear Magnetic Resonance." A talk on "High Temperature Chemistry" by Leo Brewer of UC was followed by a tour of the chemistry facilities at Cal Poly.

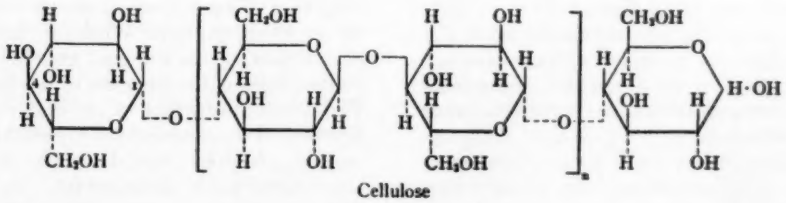
JOHN LEO ABERNETHY
Editor of PSACT Proceedings

FRESNO STATE COLLEGE
FRESNO, CALIFORNIA

The PSACT will sponsor a Summer Conference on the Teaching of Chemistry at beautiful Asilomar, on the Monterey Penninsula August 17–21, 1959. Chemistry teachers and their families from all locations are invited. Special lectures by national authorities, evening movies from foreign locations, swimming and other recreation, planned trips to nearby points of interest, and fine food will be parts of this program. Information can be procured from Sister Agnes Ann Green, Director, Immaculate Heart College, Los Angeles, California.

Chem Gems—A Cultural Pearl

Query: What famous line in Milton's "L'Allegro" is suggested by the following:



Cellulose

Answer: ". . .linked sweetness long drawn out."

KARL F. HEUMANN
Chemical Abstracts
Columbus, Ohio

Robert D. Eddy
Tufts University
Medford, Massachusetts

The Hydrogen Organ

The hydrogen organ is a superb device for lecture table demonstration. In one fascinating two-minute period, it can safely show that hydrogen is lighter than air; that hydrogen molecules move faster than oxygen and nitrogen molecules; that pure hydrogen burns quietly with a colorless, transparent flame; and that a hydrogen-air mixture is violently explosive. I have never seen this instrument described anywhere, so I do so here, wishing that I might give proper credit to its unknown designer. The Tufts model has been in the Chemistry Department for at least 20 years—so long that its origin is now shrouded in mystery. I have been told that there are similar or modified ones in use at other schools and colleges.

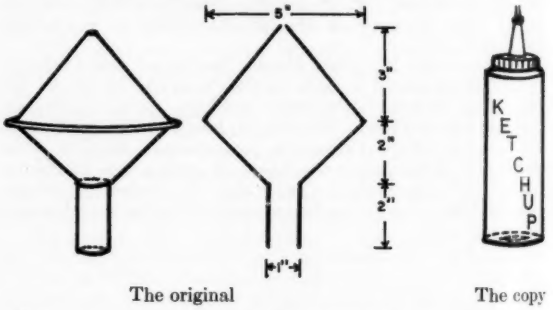
Our hydrogen organ is a hollow vessel made from two circular cones of 0.032-in. thick sheet brass fastened firmly together at the rims of their bases. A $^3/_{32}$-in. hole has been drilled at the apex of the upper cone. The lower cone has been truncated and a hollow cylindrical tube (organ pipe) 2 in. long and 1 in. in diameter has been fastened on securely.

When used, the organ is clamped firmly between two iron rings on a ring stand, then is filled with hydrogen through the lower opening. When a tank source of gas is used, the apparatus can be quickly loaded without bothering to plug the upper hole. If a slower, home-made generator is used, it is better to close this opening in some temporary way. The organ can be filled by immersing it in a pan of water, covering the upper opening with the finger, and introducing gas to displace the water. When full, it is moved a *safe distance* from the generator and lit with a match at the *upper* hole. The hydrogen rises through the upper hole and creates enough pressure to maintain a quiet, steady, colorless, and transparent flame. It can be made visible by gently beating a blackboard eraser nearby, thus introducing the brick red color of the calcium flame.

As the hydrogen burns, the organ begins to play. Air entering at the bottom sets up sound vibrations which are apparently reinforced by the organ pipe. The pitch of these vibrations will depend on the changing average velocity of the gas molecules within the vessel as the hydrogen is being replaced by air. The design of our organ is such that when it is full of hydrogen the characteristic vibration is well above the audible range. After five to ten seconds of burning, a high pitched squeal will be heard, followed by a whine of constantly descending pitch—like the wail of a siren which is slowing down. This is loud enough to be heard throughout an auditorium with more than 250 seats. When the pitch drops below the audible range, there is a moment of silence and then the flame strikes back. When the explosion limits of the hydrogen-air mixture are reached, the confined gases react with an unexpected violence. Flames spurt from the pipe, the ring stand rocks, the walls echo, and the audience, which has been leaning forward, straining to hear the descending whine of the organ, is startled.

Squeeze-bottle Modification

The squeeze-bottle organ is a less effective imitation of the original, but for those who do not know the real thing it makes an interesting demonstration. The idea



The original The copy

of using a polyethylene bottle was first suggested by George O. Johnson of Culver (Indiana) Academy. A ketchup bottle is modified by drilling a $^7/_{16}$-in. circular hole in the center of the bottom and by inserting a hollow glass tip in the top. The polyethylene tip cannot be used without protection, for the heat of the hydrogen flame softens the plastic and seals the nozzle. An inch-long, cone-shaped glass jet drawn out like a wash bottle tip serves adequately. When first ignited, the flame will be colorless, but as the glass gets hot it colors the flame yellow, making the progress of the flame easy to follow. The descending whine of the organ is apparently not a function of the shape of the vessel, nor is the organ pipe needed. It does depend on the relative sizes of the lower opening and the upper jet. As might be expected, the polyethylene absorbs most of the noise. The clear resonant song of the original metal organ is transformed to a sort of rubbery "Bronx cheer" of descending pitch.

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Chem Ed

LETTERS

EDITOR'S NOTE: We are happy to publish the following excerpts of factual information from letters commenting on the article, "The Chemical and Related Literature of Australia and New Zealand" by Dr. L. J. Stevens, J. CHEM. EDUC., **35**, 566 (1958). We assure our friends in the southern hemisphere that neither the author nor the editor intended inaccuracy. The original paper was prepared in 1957 for oral delivery; space restriction necessitated abbreviation in the version published.

To the Editor:

There are now five universities in New Zealand, comprising the University of New Zealand (a central administrative body, in Wellington, which also controls Massey and Lincoln Agricultural Colleges), the University of Auckland (in Auckland), Victoria University (in Wellington), the University of Canterbury (in Christchurch), and the University of Otago (in Dunedin). The last four universities were, until 1957, constituent colleges of the University of New Zealand. Incidentally, Lord Rutherford was a graduate of the former Canterbury University College.

Both the New Zealand Institute of Chemistry and the Waikato branch of the Royal Society of New Zealand (formerly the Waikato Scientific Association) are learned societies and not research institutions. Under learned societies might also be added the New Zealand section of the Royal Institute of Chemistry.

The *New Zealand Journal of Science and Technology* ceased publication in 1957 to make way for three new journals, *New Zealand Journal of Agricultural Research*, *New Zealand Journal of Science*, and *New Zealand Journal of Geology and Geophysics*, all of which are published bimonthly.

The Academy of Science is not a research institution but is Australia's most distinguished learned society. Its headquarters are in Canberra. The Royal Society of South Wales (not North Wales) is only one of the many State royal societies in Australia. Similarly, the Royal Australian Chemical Institute, with headquarters in Melbourne, has branches in all the Australian states and a local section in the Australian Capital Territory.

D. D. PERRIN

THE JOHN CURTIN SCHOOL OF MEDICAL RESEARCH
THE AUSTRALIAN NATIONAL UNIVERSITY
CANBERRA, A.C.T.

To the Editor:

There should be several additions to the list of Australian universities in Table 1, viz., University of Adelaide (founded 1874), Australian National University, Canberra (1946), University of New South Wales (1949), University of New England, Armidale (1954). In addition, Canberra University College (1929), and Newcastle University College (1951) provide courses to graduate level, and Monash University, Melbourne, was founded in 1958 and will commence lectures in 1960.

The article may give the unfortunate impression that scientific and industrial development in Australia and New Zealand is in its infancy, which is not true. There are several large-scale chemical manufacturers in Australia who also maintain their own research organizations, a practice which is also followed by many of the smaller firms. Some examples are Imperial Chemical Industries of Australia and New Zealand, Monsanto Chemicals, Broken Hill Proprietary, several Oil Companies, Nicholas Organization, etc. (for further information refer to the series appearing in Proceedings of the Royal Australian Chemical Institute, Vols. 24, 25 (1957, 1958).

R. P. C. POCKLEY

BALLIOL COLLEGE
OXFORD, U. K.

To the Editor:

Your excellent articles on balances by S. Z. Lewin prompt me to ask for opinions on the use of the single-pan balances for the first course in quantitative analysis. I gathered at the Chicago meeting that others have also been giving this some thought.

Traditionally in quantitative analysis we have maintained that a scientist should learn the most precise technique for the ultimate in weighing on the classical analytical balance. But, now the single-pan balance can replace the classical balance in accuracy and far surpass it in convenience. While I, too, am attached to this trusty old friend, it does seem that the two-pan balance will be a museum piece in the very near future. So, before completing the change, I should like to know if anyone has reasons for continuing their use in the quantitative analysis course. Price does not seem a real barrier because the new type serves for many more students, because of its speed, and no weight sets are needed. My brief experience with these balances in the undergraduate course shows that students have time for more chemical work per lab and are glad to avoid the tedious weighings they had to make as freshmen.

WILLIAM B. GUENTHER

THE UNIVERSITY OF THE SOUTH
SEWANEE, TENNESSEE

✦ ✦ ✦

Chem Ed

BOOK REVIEWS

Qualitative Testing and Inorganic Chemistry

Joseph Nordman, Los Angeles Valley Junior College. John Wiley & Sons, Inc., New York, 1957. xii + 488 pp. 61 figs. 73 tables. 16 × 23.5 cm. $6.25.

For those instructors who still feel that qualitative analysis is a must in first year chemistry this book offers everything that anyone could want to put into the course. The author assumes that users of the book have had a thorough grounding in general chemistry either by a full year course or a course given in two quarters.

The first thirteen chapters contain the theoretical approach to qualitative analysis by reviewing chemical equations, concentration, atoms, bonds, and molecules, in the first three chapters. Following the review, the next ten chapters deal with equilibrium and give a rather thorough discussion of complex formation. The last two chapters discuss organic reagents and metallurgy.

The remainder of the book is a laboratory manual for semi-micro qualitative analysis which has essentially the flow sheet type of conventional divisions which have been modernized by the use of organic reagents and thioacetamid instead of H_2S. One chapter is devoted to some of the less familiar elements and one is devoted to special experiments such as blow-pipe analysis, spot tests and spectrographic identifications.

The appendix contains all of the necessary tables for qualitative analysis and includes tables of equipment and chemicals necessary for the course.

This reviewer finds the absence of illustrations other than a few line drawings and a crowded format gives the feeling that the reader is involved with a handbook rather than a textbook. Should the teacher be concerned with developing analysts or technicians for industrial laboratories this book would offer an excellent training ground.

JAMES F. CORWIN
Antioch College
Yellow Springs, Ohio

Experiments in General Chemistry

Joseph B. Nordman, Los Angeles Valley Junior College and *Ernest S. Kuljian*, Los Angeles Pierce Junior College. Burgess Publishing Co., Minneapolis, 1958. iv + 155 pp. 27 figs. 12 tables. 21 × 27.5 cm. Spiral bound. $3.50.

This laboratory manual would fit practically any course in general chemistry since it contains the usual experiments with some modifications that are used to illustrate chemical principles. The presence of four demonstration type experiments which include two on the gas laws and one each on electro-chemistry and radioactivity make it somewhat different.

The report blanks are fill-in type and graph paper is included for reporting certain experiments. The authors suggest that these remain in the manual and will be graded in the laboratory before materials for the next experiment are issued.

The 26 experiments and 4 demonstrations would cover a two-quarter course in general chemistry but would be more than sufficient for one semester. It is suggested that a course in qualitative analysis furnish the remainder of the year's work in chemistry.

For large classes where grading individual laboratory notebook write-ups would be burdensome, the laboratory manual would be adequate.

JAMES F. CORWIN
Antioch College
Yellow Springs, Ohio

Introduction to Nuclear Engineering

Richard Stephenson, Associate Professor of Nuclear Engineering, New York University. 2nd ed. McGraw-Hill Book Co., Inc., New York, 1958. xi + 491 pp. 156 figs. 58 tables. 16 × 23.5 cm. $9.50.

This is the second edition of this book and represents a fairly complete revision of the material of the first edition and also incorporates considerably more material. This edition, as was the first edition, is well suited to serve as a text for either a survey class in nuclear processes or a one-year introductory course in nuclear engineering.

The first chapter, Review of Nuclear Physics, remains unchanged except for a larger selection of typical problems.

The second chapter, Nuclear Fission, has been reduced in scope in that the material on fuel types, critical mass, neutron moderation and the multiplication factor are the leading material for the third chapter on The Nuclear Chain Reaction. This third chapter has been increased in scope over the first edition to include descriptions of various power reactors presently being proposed in the United States. This includes brief descriptions of the pressurized water, boiling water, sodium graphite, homogeneous, organic moderated and fast breeder reactors.

The fourth chapter on Reactor Theory, the fifth on Radiation Shielding, and the sixth on Materials of Construction remain essentially the same and still serve as good introductory chapters in these basic areas.

At this point a new chapter has been added to the second edition on Reactor Core Design and lists the basic problems associated with reactor heat transfer, burnout heat fluxes, and hot channel factors. Also, considerations of mechanical design are discussed including mechanical and thermal stress aspects as they relate to core design.

The chapters on Reactor Instrumentation and Control and Separation of Stable Isotopes remain unchanged. The

Reviewed in this Issue

Joseph Nordman, Qualitative Testing and Inorganic Analysis
Joseph B. Nordman and *Ernest S. Kuljian*, Experiments in General Chemistry
Richard Stephenson, Introduction to Nuclear Engineering
Jay A. Young, Practice in Thinking: A Laboratory Course in Introductory Chemistry
Lloyd N. Ferguson, Textbook of Organic Chemistry
T. E. R. Singer, Editor, Information and Communication Practice in Industry
George Urdang, Carl Wilhelm Scheele—The Apothecary Chemist
Gmelins Handbuch der Anorganischen Chemie. System 3. Oxygen. Section 3: Elementary Oxygen
U.S.S.R. Academy of Sciences, The Structure of Glass
Modern Chemical Processes. Volume 5
Robert U. Bonnar, Martin Dimbat, and *Fred H. Stross*, Number Average Molecular Weights
W. Mayo Smith, Vinyl Resins
Melvin A. Cook, The Science of High Explosives
John Happel, Chemical Process Economics
James O. Osburn and *Karl Kammermeyer*, Money and the Chemical Engineer
Gmelins Handbuch der Anorganischen Chemie. System 42, Zirconium; System 43, Hafnium

later chapter has included a new section on the production of heavy water. The chapter on Chemical Separation and Processing has incorporated the chapter of the first edition entitled Separation Techniques of Nuclear Engineering. It includes design concepts of hot cells, dry boxes and manipulators.

The last chapter of the second edition is an entirely new chapter on Thermonuclear Power, and gives the theoretical basis for these processes. This is certainly a needed addition to complete a text on nuclear engineering.

In summary it can be stated that the second edition of this text brings together much more information than was available at the time of printing of the first edition. Much of this added information was released at the 1955 Geneva Conference. Already the second such conference (1958 Geneva Conference) has been held this year and additional information has been made available. Thus, in this rapidly expanding field of nuclear engineering, this second edition will certainly help to build the framework upon which subsequent editions will be required to bring the text continually up-to-date.

RALPH BALENT
Atomics International
Canoga Park, California

Practice in Thinking: A Laboratory Course in Introductory Chemistry

Jay A. Young, King's College, Wilkes-Barre, Pa. Prentice-Hall, Inc., Englewood Cliffs, N. J., 1958. xviii + 92 pp. 12 figs. 22.5 × 28 cm. Spiral bound. $2.95.

The student using this laboratory manual is not told to verify the facts and theories of chemistry; he is required to discover them. To expedite the process of discovery a chemical problem is assigned. The student is required to (1) plan and carry out an attack on the problem, (2) invent an explanation for the phenomena observed, (3) devise and carry out experiments to verify or nullify his explanation, and finally (4) understand the problem in terms of the best modern theory. There are no equations or detailed procedures in the manual. These must be accumulated by working in the laboratory and by reading the literature.

In requiring the student to invent testable explanations for phenomena observed, this book represents an attempt to "revive" the essence of science and science teaching. All too many of the modern textbooks give the student the feeling that the theories presented are facts rather than imaginary devices used to explain.

To teach a course of the kind outlined by Dr. Young might require more effort than many can contribute to a first year course, but some of his ideas are worth detailed consideration. It is this reviewer's opinion that this laboratory manual should be "required reading" for chemistry teachers.

L. CARROLL KING
Northwestern University
Evanston, Illinois

Textbook of Organic Chemistry

Lloyd N. Ferguson, Professor of Chemistry, Howard University. D. Van Nostrand Co., Inc., Princeton, N. J., 1958. xviii + 618 pp. 16 × 23.5 cm. $7.50.

The approach of this text is direct and follows the classical subdivision of subject matter. The style is clear and friendly. Chapters are short and exercises and literature citations generally good and well placed. Average students will find the text helpful and there is enough material to challenge the reasonably good student, but not the exceptional one.

The teacher who uses this text will find it easy to schedule his lectures to cover the one year course, and, by relying heavily on the text, will be able to place emphasis in class on selected points, rather than feeling that he must transmit to the student a set of notes to serve as the major basis for the course.

There are some innovations in this book which are of value, such as the review sections for the first and second semester's work, and the appendix, which demonstrates the solutions of diverse problems.

Dr. Ferguson's presentation of the physical aspects of organic compounds is modern and useful. "Lasso chemistry" is still used considerably to show which parts of reactants are eliminated, etc., but this is balanced by a fair amount of electronic and mechanistic interpretation. The author's treatment of light absorption (his special interest) and optical activity is good and will help the student to grasp these aspects. The practical and medicinal aspects of organic chemistry are also well brought out and natural products and biochemical interests are adequately represented.

Teachers who present general courses of organic chemistry to a broad spectrum of students and who are not looking for a radically different book should find Dr. Ferguson's book of interest for consideration.

NORMAN KHARASCH
University of Southern California
Los Angeles

Information and Communication Practice in Industry

Edited by *T. E. R. Singer*, Technical Information Consultant and Program Chairman of Division of Chemical Literature, ACS. Reinhold Publishing Corp., New York, 1958. vi + 304 pp. 16 × 23.5 cm. $8.75.

This slick-paper book is a collection of 18 articles on handling and communicating technical information and more or less related subjects. The first chapter, entitled The Industrial Information Department, does an adequate job of describing both the organization and operations of a mature industrial technical-information center. Most of the subsequent chapters deal in greater detail with the principal functions of a information staff. The emphasis in many of them is on counseling beginners in the field, rather than on presenting a cross section of how these operations are performed in industry.

Unfortunately, the chapters neither follow in logical sequence nor provide an integrated and balanced picture. The chapter on Linguistics, Language and Terminology is more entertaining than apropos. That on Mechanical Aids to the Effective Presentation of Technical Papers is not especially entertaining. Paradoxically, not a single illustration appears in the chapter on technical illustrations. The amount of detail diverges widely from chapter to chapter, and also noticeable repetition occurs. Under these circumstances, the index is extraordinarily helpful.

The book will be most useful to an organization about to establish an information center, in particular as a reference for new recruits in information work who require orientation in the specialized activities. Good bibliographies accompany each chapter.

E. L. D'OUVILLE
Standard Oil Company (Indiana)
Chicago, Illinois

Carl Wilhelm Scheele—The Apothecary Chemist

George Urdang, Emeritus Professor, University of Wisconsin. American Institute of the History of Pharmacy, Madison, Wis., 1958. 35 pictures. 66 pp. 20.5 × 28 cm. Paper bound. $2.50.

Carl Wilhelm Scheele (1742–1786) is a formidable candidate for the honor of the most fruitful chemist. He, like Mozart in music, touched all branches of his field in a life that covered only a few decades and left immortal traces of his activities. There is no full-length biography of this gifted chemist-apothecary but essays concerning his life and achievements are many. The present sketch was first issued in 1942 and has been but slightly modified in this edition. As stated in the subtitle, the illustrations are an integral part of the text and hence are provided with ample legends. For the most part these illustrations are taken from the excellent Scheele biography by Otto Zekert issued between 1931 and 1935 by the Gesellschaft für Geschichte der Pharmazie.

The present author has done his work well. He has given in 10 pages an excellent condensed account of Scheele's life and accomplishments written in a readable and interesting style. Since the volume was sponsored by pharmaceutical houses and pharmacists, it is not surprising that stress is laid on the fact that Scheele came into chemistry from pharmacy and spent his entire life, from his apprenticeship on, in various apothecary shops. Scheele's own words give evidence of his pride in his profession: "I am doing my chemical research only as a sideline in order not to neglect my duty in my apothecary shop."

A special section (2 pages) is devoted to a summary of Scheele's achievements. This is taken predominantly from the essay (1894) included in T. E. Thorpe's "Essays in Historical Chemistry." A

very useful "Timetable of Experiments as Reported in Scheele's Own Letters and Notes" occupies the last 12 pages.

The reviewer recommends that this volume be made available to all chemists from the high school level up. It is not only full of worthwhile information but it will serve to show the wisdom of the old German adage that a golden cage is not essential to a flood of melody from the bird.

RALPH E. OESPER
University of Cincinnati
Cincinnati, Ohio

Gmelins Handbuch der Anorganischen Chemie. System No. 3. Oxygen Section 3: Elementary Oxygen

Edited by the Gmelin Institute under the direction of *E. H. E. Pietsch*. 8th ed. Verlag Chemie, GmbH, Weinheim Bergstr., 1958. xi + 518 pp. 100 graphs. 17.5 × 25.5 cm. Paper bound, $67.92.

This further section of the eighth edition of Gmelin's Handbook has been assembled with the usual care and thoroughness of the Gmelin Institute.

After an initial section on the preparation of oxygen and the separation of its isotopes, an extensive section of 275 pages presents the physical properties of O, O_2, O^- as well as the less common forms of the element. The difficulties of an atomic weight scale based on oxygen are discussed. Recent material is included in the section on optical properties of oxygen, especially microwave studies. Magnetic and electrical properties are also treated.

The chemical reactions of oxygen are not covered since they are treated in the volumes dealing with other elements. This section is replaced by a lengthy treatment of reactions of H_2–O_2 and H_2–air mixtures. A full record of experimental results and proposed explanations is given for these reactions under all kinds of experimental conditions.

This further volume confirms the great utility of the Gmelin Handbook for those who can afford it.

THOMAS E. FERINGTON
The College of Wooster
Wooster, Ohio

The Structure of Glass

U.S.S.R. Academy of Sciences, Institute of Silicate Chemistry. Translated by *E. B. Uvarov*. Consultants Bureau, Inc., New York, 1958. 291 pp. Many figs. 22 × 28 cm. $20.

This book presents the proceedings of a Symposium on Glass Structure held in 1953 in Leningrad. The title states the unifying theme to which all of the 73 papers, communications, and discussions contribute, but the reader will find it more valuable as an index of the varied and active work going on in Russia at the present time on all phases of glass science than as the statement of any final established structure of glass.

Much space is devoted to evidence and arguments supporting the crystallite theory of glass structure which in most cases is regarded as entirely different from the Zachariasen random network theory. However, some of the Russian scientists feel that the theories must be combined. Thus G. B. Bokü states "There are no irreconcilable differences between the crystallite and the Zachariasen theories—they are two aspects of the same question. Glass contains regions of greater order, which can be termed crystallites, since the repeat periods correspond to the repeat periods found in crystalline silicates, and regions of less order. But even in the ordered regions the degree of order should be less than in silicate crystals. The atoms which form the oxygen bridges linking these two types of regions—ordered and disordered—cannot, in principle, be attributed to either type of region, so that we have a continuous transition and there are no phase boundaries between the crystallites."

These remarks present what appears to be the general conclusion reached by a majority of more than 500 participants in the Conference. However, there remained considerable differences of opinion between different schools. The great need for further work is generally recognized, particularly the need for developing new methods for more precise determination of the size and shape of the ordered regions in glasses, for determination of the composition of these regions, of the nature and degree of distortion of the crystallite structure relative to the crystals of the corresponding compounds, and for estimation of the proportions of regions of physical and chemical order in the total volume of the glass.

One of the principal groups of papers concerned the sodium borosilicate glasses and the microporous structures which can be obtained from them by heat treatment and leaching.

The applications of X-rays, Raman spectra, infrared spectra, Rayleigh scattering, and electron microscopy were treated in various papers. Viscosity, dielectric loss, electrical conductivity, thermal expansion, heat capacity, and chemical resistance were investigated from the point of view of glass structure. Particularly interesting was a paper on Structural Changes of the Refractive Index of Glass at Temperatures below 300°C.

Unfortunately, because of the vast amount of work summarized at the Conference, little attention could be given to experimental details. It is difficult to judge the reliability of results in many cases. In the discussion section it is evident that the Russian authorities on glass are far from unanimous in their interpretation of experimental work.

The Glass Division of the American Ceramic Society and the National Science Foundation are to be congratulated for making this inspiring collection available to those who do not read Russian. It seems certain that many will indeed be enticed by it to become even better acquainted with Soviet science.

C. H. GREENE
State University of New York
Alfred

Modern Chemical Processes. Volume 5

Editors of *Industrial and Engineering Chemistry*. Reinhold Publishing Corp., New York, 1958. v + 154 pp. Many figs. and tables. 21.5 × 29.5 cm. $5.

This volume completes ten years of reprinting the I.E.C. Staff-Industry Collaborative Report which usually appears monthly in *Industrial and Engineering Chemistry*. Previous volumes appeared in 1950, 1952, 1954, and 1956, so the 1958 volume reprints the article that appeared in the years 1956 and 1957.

During this two year period 14 reports appeared—less than in previous periods due to stricter editing. Of these 14 reports, ten deal with inorganic technology and four with organic technology. A detailed index is included.

The articles are replete with flowsheets, diagrammatic drawings, tables of data, and equations for the process reactions. Both instructors and students will find this volume essential to bring their textbook material up-to-date and extent it into new areas, like uranium from gold wastes or wet process phosphoric acid.

KENNETH A. KOBE
The University of Texas
Austin

Number Average Molecular Weights

Robert U. Bonnar, Martin Dimbat, and *Fred H. Stross,* Shell Development Co. Interscience Publishers, Inc., New York, 1958. x + 310 pp. Many figs. and tables. 16 × 23.5 cm. $7.50.

Not very long ago, determinations of molecular weights were confined to academic laboratories where they served in the elucidation of a structure or in the study of the behavior of solutions. Today they have become routine tools of industrial research and thence spread into control laboratories and even into trade specifications. At the same time their principal field of application has become the characterization of mixtures of similar molecules such as plastics or petroleum fractions. In this field the single number given by a molecular weight determination becomes an average of the values characterizing the individual molecules of the mixture. The value of this average depends on the method used in determining it.

The present volume is concerned only with the family of methods which yield the number-average molecular weight, i.e., the cryoscopic, ebulioscopic, osmotic pressure, vapor pressure lowering, gas density, and end-group analysis methods. About 80% of the book is devoted to the first three methods and to their interpretation. These are the preferred methods of the authors, and the others are surveyed rather briefly.

This is not a book put together with scissors and paste in a library cubbyhole. The reader can constantly feel that the authors write from their own laboratory experience and that their advice is based

(Continued on page A314)